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ABSTRACT

Because of their applications in fuel cell electrochemistry and in problems such as the electrochemical recovery of breathing oxygen from carbon dioxide, the chemistry and electrochemistry of carbonates in the molten state have been the subject of considerable attention in the period of the past two decades. The concern of the present communication is a survey of the recent contributions in this area, particularly relative to the classification of molten carbonates as solvent systems and as electrolytes. Thermodynamic and transport properties are first considered; a development of the acid-base concept relative to molten carbonates is next examined, and its application to corrosion chemistry and the solubility of oxides in molten carbonates is illustrated. The electrolysis of molten carbonates (cathodic phenomena) is discussed to illustrate the thermodynamic method in this area. A compilation of salient results in the area of molten carbonates is reported as an Appendix of this communication.

General Features Of Molten Salt Solvent Systems

Fused salts exist as stable liquids over wide ranges of temperatures. A comparison of some general properties of such liquids with water and carbon tetrachloride, two well known ambient temperature solvents, is shown in Table 1. The melting points and boiling points define the limits of usefulness of a particular solvent under ordinary pressure conditions. Eutectic mixtures are frequently used to attain the molten state at somewhat lower temperatures, both to increase the liquid state range and to minimize the problems of ''container chemistry'' or corrosion in such systems. The compositions and melting points of carbonate eutectics and some of the more popular eutectics of other salts are summarized in Table 2 and Fig. 1.

Related to the melting points are two further physical constants which in themselves relate to the energy necessary to bring about the change in the state from the solid to the liquid, and from the liquid to the vapor, namely the entropies of fusion and vaporization respectively. The entropy of vaporization (the ratio of heat vaporization to the absolute boiling point) is known as the Trouton Constant[1], which usually has a value of about 21.5 for normal liquids[2]. Use

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(1) F. Trouton; Phil. Mag. 18 (5), 54 (1884).

(2) Where the value of Trouton's Constant is higher, it is considered evidence that molecules of the liquids are associated into larger aggregates; for an ionic melt, this would imply ion-pairs and/or larger aggregates.

of this empirical criterion has to date been largely limited to ambient temperature solvent systems; inspection of the values for ΔS_{vap} (Table 1) shows that it appears equally informative, in the first approximation, as a probe for the degree of association in molten salts. The nature of $ZnCl_2$ in the molten state has been the subject of a series of studies by the techniques of high temperature Raman spectroscopy[3-5]. The spectral data clearly support the existence

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(3) W. Bues; Z. anorg. allgm. Chemie, 279, 104 (1955).

(4) D. E. Irish and T. F. Young; J. Chem. Phys., 43, 1765 (1965).

(5) J. R. Moyer, J. C. Evans, and G. Y. S. Lo; J. Electrochem. Soc., 113, 158 (1966).

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of associated species in the molten state of $ZnCl_2$ (larger aggregates as a form of $(ZnCl_2)_n$ ''polymer''[6], as well as discrete molecules

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(6) The polymer, formulated as $(ZnCl_2)_n$, undoubtedly is an aggregate in which the tetrahedron, $ZnCl_4^{-2}$, is a recurring unit, and with the neighboring tetrahedra linked by shared chlorides, much as in the crystalline state.

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of $ZnCl_2$ or $ZnCl^+$, $ZnCl_3^-$, $ZnCl_4^{-2}$ ...). In contrast to this, the spectral data for $HgCl_2$ in the molten state are understood[7] if the species formed on fusion are discrete molecules, i.e. molecular mercuric chloride, with little or no evidence for higher aggregrates

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(7) G. J. Janz and D. W. James; J. Chem. Phys., 38, 902 (1963).

(c.f. normal liquids). The markedly higher viscosity[8] of $ZnCl_2$ (Table 1) is further independent support for the associated nature of $ZnCl_2$ in the molten state.

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(8) J. D. Mackenzie and W. K. Murphy; J. Chem. Phy. 33, 360 (1960).

Relative to $HgCl_2$, the studies of Janz and MacIntyre[9] and Bockris, Crook, Bloom and Richards[10] on the structure and properties of the mercuric halides have been informative. A high degree of covalency is retained in the molten state on fusion, and the small

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(9) G. J. Janz and J. D. E. MacIntyre; Annal. New York Acad. Sci., 79, 709 (1960); J. Electrochem. Soc., 109, 842 (1962).

(10) J. O'M. Bockris, E. H. Crook, H. Bloom, and N. E. Richards; Proc. Toy. Soc. A255, 558 (1960).

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but finite electrical conductance was attributed to ionic species from a self-dissociation of this ''molecular'' type melt. From a study of the temperature dependence of the electrical conductance, and a comparison of the energetics of bond dissociation energies, heats of ionizations, the following self-ionization scheme was advanced[9].

$$2HgCl_2 \rightleftarrows HgCl^+ + (HgCl_3)^-$$

or $\underline{1}$

$$3HgCl_2 \rightleftarrows 2HgCl^+ + (HgCl_4)^{-2}$$
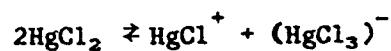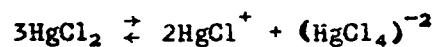
in which the enthalpy change due to the ''complex-anion'' formation compensates for the high heat of ionization required for producing

free $HgCl^+$ and Cl^-. Molten mercuric chloride may thus be classified as a high temperature non-aqueous ''water-analogous'' solvent system. The approximate degree of ionization, α, for molten $HgCl_2$ has been estimated[9] as 3.5×10^{-5} at 280°C (c.f. H_2O, 10^{-7}).

It follows from the self-ionization processes[1] and the parent-solvent concept of non-aqueous solvent systems[11], that in molten mercuric halides all substances yielding the entities HgX^+ and HgX_3^- or HgX_4^{-2} are, respectively, acid-analogous and base-analogous compounds. Solute- solvent reactions (corresponding to the formation of acids from nonmetal oxides and bases from metal oxides) such as:

$$HgSO_4 + HgCl_2 \rightarrow (HgCl)_2SO_4$$

and
$$\underline{2}$$

$$2KCl + HgCl_2 \rightarrow K_2(HgCl_4)$$
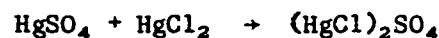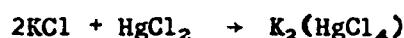
account for the solubility as ''electrolytes'' of various mercuric salts and the alkali chlorides in molten mercuric halides; the neutralization analogous reaction, such as the titration of $HgSO_4$ and KCl, both dissolved in molten $HgCl_2$:

$$HgSO_4 + 2KCl \rightarrow K_2SO_4 + HgCl_2 \qquad \underline{3}$$
(acid analog)　(base analog) (salt)
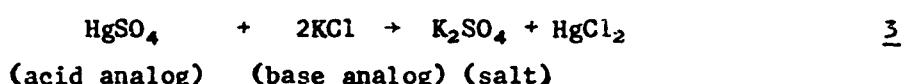
may be monitored with the classical conductometric techniques, modified for application to moderately high temperature liquids. Cryoscopic and conductometric measurements[12], and spectroscopic studies[13]

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(11) L. F. Audreth anu J. Kleinberg; ''Non-Aquecus Solvents''; J. Wiley and Sons, Inc., N. Y. (1953).

(12) E. Beckman, Z. anorg. allgem. Chem., 55, 175 (1907); H. Foote and N. Martin, Amerc. J. Sci., 41, 451 (1909); G. Jander and K. Broderson; Angew. Chemie., 62, 264 (1950); Z. anorg. Chemie; 261, 261 (1950); 262, 33 (1950); 264, 57, 76, 92 (1951); 265 117 (1951); Z. anal. Chemie; 133, 146 (1951). G. J. Janz and J. Goodkin; J. Phys. Chem., 64, 808 (1960).

of fusion, ΔS_f. Inspection of the fusion parameters (Table 1) shows that for compounds containing ions of the inert gas structure (i.e. NaF, NaCl), ΔS_f is approximately 3 e.u. per g. ion. The Temkin model for the liquid state of such melts[15] has been a useful first approximation in the thermodynamic studies of molten mixtures of such salts.

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(15) M. Temkin; Acta Physicochim. U.R.S.S. (Engl) 20, 411 (1945).

In this model it is assumed that the melts are completely ionized, and that statistically the anions and cations are randomly distributed relative to like-ion species, but that the nearest neighbors of anions are cations, and vice-versa (i.e. rather as though a blurred memory of the first coordination shell of the crystal lattice persists in the molten state[16]). For ionic compounds with polyatomic ionic constituents, e.g. nitrates, and carbonates, and also for compounds such as $ZnCl_2$, the interpretation of the entropy of fusion is a more complex problem[17], requiring due cognizance of possible contributions

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(16) See for example the results of X-ray and neutron diffraction studies of the alkali halides, i.e. H. A. Levy and M. A. Danford, Chapt. 2, Molten Salt Chemistry (M. Blander, Ed.), Wiley-Interscience, Publ. N.Y. (1964).

(17) A. R. Ubbelohde; Melting and Crystal Structure; Clarendon Press, Oxford (1965).

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from additional factors such as vibrational entropy, changes of association or chemical bonding, and randomization within the polyatomic

species, i.e. configurational entropy. The discussion of this problem falls outside the scope of the present intent of this communication. The high electrical conductance of the melts from such ionic salts (NaF, $NaCl$, $NaNO_3$, Na_2CO_3, Table 1) classifies these types of solvents as molten electrolytes rather than as high temperature water-analogous systems; it is of interest to examine briefly the properties of the nitrates and carbonates relative to those of the alkali halides from this viewpoint.

In general it is observed for such molten electrolytes that the electrical conductance and viscosity for a limited range of temperature may be expressed by the exponential equations:[18]

$$\cdot = A_\Lambda e^{-E_\Lambda/RT}$$

and   6

$$\eta = A_\eta e^{E_\eta/RT}$$

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(18) The equivalent conductance, Λ , for a molten electrolyte is given by $\Lambda = \dfrac{M\kappa}{\rho}$, where M and ρ are the equivalent weight of the salt and the density of the melt; this follows from the classical defin-

$\Lambda = \dfrac{1000\,\kappa}{C}$, when it is applied to the upper limit of concentra-

tion for the electrolyte, i.e. the ''zero-dilution'' limit, or the state of the single-salt melt as the electrolyte.

In Table 4 are summarized the values for the exponential constants, E_Λ and E_η, the activation energies for electrical conductance and viscosity respectively, for the alkali metal halides, nitrates, and carbonates[19].

(19) G. J. Janz, F. W. Dampier, and P. K. Lorenz; ''Molten Salts: Electrical Conductance, Density, and Viscosity Data'' National Standards Reference Data Report; U.S. Dept. Commerce (in press, 1967).

Inspection shows that the activation energies for corresponding halides, nitrates and carbonates are quite similar in magnitude, although there are small variations. The electrical conductance of the nitrates is nevertheless considerably less than that of the corresponding halides and carbonates (e.g. Table 1, NaF, NaCl, $NaNO_3$, and Na_2CO_3). If the equivalent conductances of molten nitrates are extrapolated to the same temperature range as for the halides and carbonates (i.e. 800° - 900°C) the values, as shown in Table 5, are qualitatively quite comparable to the conductances of higher melting salts. The lower values of the transport properties of the nitrates relative to the corresponding chlorides, thus, are understood, in large part, due to the different ''kinetic energy content'' of the liquids. The term ''low-energy melts'' has been advanced[20] accordingly for the liquids from low melting ionic salts, such as nitrates.

(20) G. J. Janz and D. W. James; Electrochimica Acta 7, 427 (1962).

The nearly invariant values of E_Λ for the molten nitrate and carbonate series of salts (i.e. about 3.5 and 4.5 kcal equiv^{-1}, respectively, Table 1) is in marked contrast for the values of E_Λ for the corresponding series of salts as fluorides (c.f. 1.8 for LiF and increasing to 3.3 for CsF), chlorides (2.0, 5.1), bromides (2.1, 5.5)

and iodides (1.3, 5.5). The trend in the alkali halide series has been attributed to differences in the cationic mobilities. In the nitrate and carbonate series (in which, in contrast to the situation in the alkali halides, the nitrate and carbonate ions have at least three anion-cation interaction sites of distinctly different force-field intensities[21-23]), the invariancy of E_Λ has been attributed to an aggregate cooperative transport mechanism which effectively damps out the differences in cationic mobilities[24,25]. The contribution of Lantelme and Chemla[26] using diffusion data and transport experiments, is a further advance in this area. From the

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(21) J. Zarzycki; Disc. Faraday Sci., 32, 38 (1962).

(22) K. Furakawa; ibid., 32, 53 (1962).

(23) G. J. Janz and A. T. Ward; Electrochimica Acta, 10, 849 (1965).

(24) G. J. Janz and M. R. Lorenz; J. Electrochem. Soc. 108, 1052 (1961).

(25) G. J. Janz and F. Saegusa; ibid., 110, 452 (1962).

(26) F. Lantelme and M. Chemla; Electrochimica Acta, 10, 663 (1965).

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simultaneous competition of Li^+, K^+ and Na^+ for the formation of ion-pairs (molecules) and higher aggregates, and deviations from the Nernst-Einstein relationship in molten nitrates, support is gained for the viewpoint that the Na^+ and K^+ ions are ''kinetically free'' species whereas a significant fraction of the Li^+ ions are associated with the nitrate ions in such melts (e.g. 280°C, 27%

$[LiNO_3]°$ and 14% $[Li_2NO_3^-]^+$). Spedding and Mill[27] have advanced similar concepts to account for the variation observed in the value of E_D (the energy of activation for diffusion) with variation in melt composition in binary and ternary mixtures of alkali metal carbonates in the molten state. While the interpretations are still essentially qualitative, it is apparent that molten nitrates, carbonates (and related melts with well defined polyatomic ionic species) are a significant area for attention relative to cooperative effects in the treatment of fused salts as molten electrolytes.

(27) P. L. Spedding and P. Mills, Electrochem. Soc., 112, 594 (1965); 113, 599 (1966); J. Phys. Chem., 70, 4077 (1966).

Acid-Base Relationships in Molten Carbonates

Acid-base relationships in high temperature non-aqueous media are of great practical value. Many metal fluorides and oxides dissolve in an excess of molten alkali fluoride; the fluoride ion here acts as a strong base, the small radius of the fluoride ion (1.36 Å) undoubtedly contributing to the formation of extremely stable complexes of relatively low ionic weights, with the formation of molten mixtures of low viscosity and high electrical conductance. With reference to silicate melts, for example, the fluoride, (acting as an anion base), is an effective depolymerizing agent owing to its inability to act as a bridging group between two silica tetrahedra.

The use of fluxes in the opening-up of ores illustrates a further
practical application of such relationships; for acidic ores, fluxes
such as NaOH, Na$_2$CO$_3$, NaF, CaCO$_3$, CaO, KF are generally used (these
are high temperature bases); for basic ores, silica borax, bisulfate,
pyrosulfate,(i.e. high temperature acids) are used. Some recent
advances in the area of extractive electrolyses of pure metals, and
of alloys, and for the formation of metal borides and new silicon
borides, largely from the Grenoble and Madrid schools of high tem-
perature electrochemistry[28] are summarized in Table 6.

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(28) Refer Table 6, footnote reference i-vii.

The acid-base concepts specifically applicable to oxide systems
are those proposed by Lux[29], and further developed by Flood and
Forland[30]. A base is defined as an oxide ion donor, and an acid

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(29) H. Lux; Z. Elektrochemie, 45, 303 (1939).

(30) H. Flood and T. Forland; Acta Chem. Scand., 1, 592, 781, 790 (1947).

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as an oxide ion acceptor in accord with the relations:

$$\text{acid} + O^{-2} \rightleftharpoons \text{conjugate base}; \quad K_A = \frac{(\text{base})}{(\text{acid})(O^{-2})}$$

and   7

$$\text{base} \rightleftharpoons O^{-2} + \text{conjugate acid}; \quad K_B = \frac{(O^{-2})(\text{acid})}{(\text{base})}$$
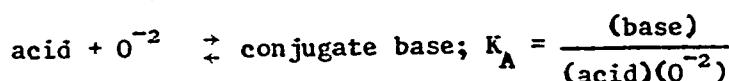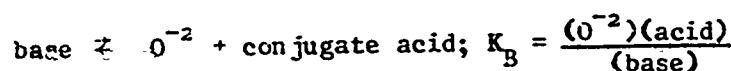
Acid-base relationships in such oxide systems involve the transfer
of the oxide ion from one state of polarization to another in which

it is more highly polarized. The chemistry and electrochemistry

of the oxidation-reduction reactions in molten carbonates[31] have

been the subject of a series of communications from this acid-base

viewpoint in the past decade, particularly with reference to high

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(31) For applications of the Lux acid-base principles in molten ni-
trates, see; F. R. Duke and M. L. Iverson, J. Amer. Chem. Soc.,
80, 5061 (1958); F. R. Duke and S. Yamamoto, ibid. 81, 6378
(1959); F. R. Duke and W. W. Lawrence, ibid., 83, 1269 (1961);
I. Slama, Collec. Czech. Chem. Commun. 28, 985 (1963); A. M.
Shamis El Din and A. A. Gerges; Electrochimica Acta, 9, 613
(1964); R. N. Kust, Inorg. Chem., 3, 1035 (1964); and A. M.
Shamis El Din and A. A. El Hosary; J. Electroanal. Chem. 9,
349 (1965).

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temperature fuel cells[32-36], and the electrochemical recovery of

breathing oxygen from carbon dioxide[37-40]. In extending the Lux-

Flood concepts to molten carbonates, it is possible to define a

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(32) J. Dubois; Ph.D. Thesis; Fac. Sci. Univ. Paris (France) (1964).

(33) M. D. Ingram and G. J. Janz; Electrochimica Acta; 10, 783 (1965).

(34) N. Busson, S. Palous, R. Buvet, and J. Millet; Compt rendu Acad.
Sci. Paris, 260, 6097 (1965); 26, 720 (1965).

(35) H. E. Bartlett and K. E. Johnson; Canadian J. Chem., 44, 2119
(1966).

(36) N. Busson, S. Palous, J. Millet, and R. Buvet; Electrochimica
Acta, 12, 0000 (1967).

(37) R. E. Shearer, J. C. King, and J. W. Mausteller; Aerospace
Medicine, 33, 213 (1962).

(38) H. W. Chandler and W. Oser; Technical Documentary Report No.
MRL-TDR-62-16; U.S. Air Force Research Command, Washington,
D. C. (1962).

9) M. D. Ingram, B. Baron, and G. J. Janz; Electrochimica Acta, 11, 1629 (1966).

(40) W. E. Arnoldi, Chapt. 4, "Atmosphere In Space Cabins and Closed Environments" (K. Kammermeyer, ed.); Appleton-Century Crafts, Publ. N. Y. (1966).

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function, analogous to pH, and which expresses the acidity of the system. It is known that the dissociation of the carbonate ion gives rise to the well-defined acid-base behavior:
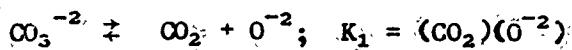
$$CO_3^{-2} \rightleftarrows CO_2 + O^{-2}; \quad K_1 = (CO_2)(O^{-2}) \qquad \underline{8}$$

where for K_1, the chemical potential of CO_3^{-2} is assumed to be invariant. If the solubility of CO_2 in molten carbonates can be expressed by Henry's Law, it follows that the equilibrium constant simplifies to:

$$K_2 = \pi_{CO_2} (O^{-2}) \qquad \underline{9}$$

where π_{CO_2} is the partial pressure of CO_2 under equilibrium conditions, $K_2 = (K_1 K_H)$, and K_H is the Henry's Law Constant. From eq. 8 it follows that an acidity function, quite similar to the pH concept of aqueous solution chemistry, may be defined for molten carbonates. Thus if the oxide ion and CO_2 activities are expressed by the two p functions:

$$pO^{-2} = -\log(O^{-2}) \text{ and } pCO_2 = -\log(CO_2) \qquad \underline{10}$$

then:

$$pK_1 = pCO_2 + pO^{-2} \qquad \underline{11}$$

and either of the two p functions may be used as a measure of the acidity, and pK defines the domain of acidity in the molten carbonate solvent system.

Domains of Acidity in Molten Carbonates: Two conventions have been advanced for establishing the domains of acidity in molten carbonates, one in which the mole fraction concentration scale and the molten oxides as reference states are used[33], and the other in which the molarity concentration scale is used[32,34], and as reference states, two solutions with the O^{-2} and the CO_2 concentrations, respectively, at 1 mol l^{-1}. These may be illustrated as follows.

If the carbonate – CO_2 dissociation equilibrium (eq. 8) is expressed as:

$$M_2CO_3 {}_{(liq.)} \rightleftarrows CO_2 + M_2O {}_{(liq.)} \qquad \underline{12}$$
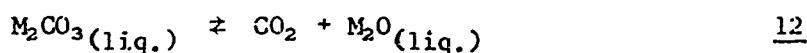
then pK can be gained from a knowledge of the free enthalpy change for the reaction, i.e.:

$$\Delta G^o = \Sigma \Delta G^o_{prod} - \Delta G^o_{f M_2CO_3(liq.)} = -2.3RT \log K_1 \qquad \underline{13}$$

Thus for the ternary eutectic mixture, if it is assumed in the first approximation that the free enthalpies of dissociation for the single salts are additive in the mixture[33,41], the value of –11.0 is predicted for K_1 at 600 °C, i.e.:

$$pO^{-2} + pCO_2 = 11.0 \qquad \underline{14}$$

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(41) G. H. J. Broers; Ph.D. Thesis; Univ. Amsterdam (1958).

If the pure molten oxide defines the reference state for unit O^{-2} ion activity, i.e. the basic limit of the acidity scale, the domain of acidity for the ternary eutectic melt at 600 °C simply is $pCO_2 = 11.0$.

Some of the acidity values predicted[33,39] in this manner for molten carbonates are summarized in Table 7a. Since the thermal dissociation of carbonates is exothermic, one predicts that the range of acidity (as measured by pK_1) decreases as the temperature increases; inspection of the results for the ternary eutectic shows that the domain of acidity decreases from 11.0 at 600 °C to 8.5 at 750 °C. Comparison of the three molten carbonate systems, Li_2CO_3, $(Na,K)CO_3$, and the ternary eutectic mixture, shows that acidities change markedly; thus at 750 °C, the binary $(Na,K)CO_3$ melt shows a much lower affinity for oxide ions than Li_2CO_3 as a single-salt melt. The calculated acidity scales should be useful for the estimation of shifts in the potential of electrodeposition on changing from one solvent to another.

The second convention[32,34] adopts, as reference states, two molten carbonate solutions, namely one having oxide ions at a concentration of 1 mol l^{-1} (i.e. $(O^{-2}) = 1.0$), and the second with the dissolved CO_2 at 1 mol l^{-1} (i.e. $(CO_2) = 1.0$). This follows general practice of ambient temperature dilute solution chemistry. To establish the domain of acidity, experimental CO_2 solubility data are essential. Thus for the ternary carbonate eutectic, it was established[32] by thermogravimetric studies that the solubility of CO_2 obeys Henry's Law if the oxide concentrations in the solvent are low, i.e.,

$$\pi_{CO_2} = 0.1 \ (CO_2) \qquad \underline{15}$$

From this it follows readily that the upper range of acidity is defined by the relation:

$$pO^{-2} = pK_1^{\ddagger} - 1.0 \qquad \underline{16}$$

It should be noted that $K_1^{\ddagger}$ differs from K_1 in the preceding practice, the units for concentration now being on the molarity scale. To establish the basic limit of the acidity scale, a series of carbonate melts containing varying amounts of O^{-2} were investigated by constant current potentiometry; it was thus established that pO^{-2} = 6.0 when the partial pressure of CO_2 is 1 atmos. above the ternary eutectic at 600 °C. It follows from eq. 16 that $pK_1^{\ddagger}$ = 7.5 units of acidity on the scale thus defined. The results established by this convention are summarized in Table 7b.

If due cognizance is taken of the differences in the concentration scales in the two conventions, it can be readily shown that the thermodynamically predicted acidity is $10^{-3.7}$ less than the acidity on the molarity concentration scale for the ternary eutectic at 600 °C. This may be attributed in part to the neglect of possible solvation interactions in the thermodynamic treatment. The molarity acidity scale has some advantages in work with molten carbonate systems as normally encountered since the oxide content generally falls in the range of 1 molar or less.

Precipitation Reactions: Two possibilities can be distinguished, depending on whether the solute is acidic or basic, i.e.:

$$acid^* + CO_3^{-2} \;\rightleftarrows\; CO_2 + base$$

and   17
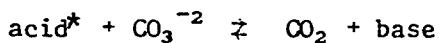
$$base^* + solvent \;\rightleftarrows\; O^{-2}_{solvated} + acid$$
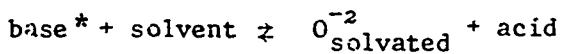
Inspection shows that strong acids (e.g. acid*) will displace the

equilibrium to the right; it follows that an acid stronger than CO_2 cannot exist in molten carbonates; from the same viewpoint, the addition of a strong base (e.g. base *) will lead to quantitative formation of O^{-2} (solvated) in the molten carbonate solvent system. The possible precipitation or dissolution reactions for various oxides in contact with molten carbonates may be examined from this thermodynamic viewpoint. The appearance of a solid oxide will be governed by the equilibrium:

$$M_2CO_3 \rightleftarrows M_2O + CO_2; \quad Kp = \frac{(CO_2)(M_2O)_s}{(M_2CO_3)_1} \qquad \underline{18}$$
$$(\text{liq.}) \quad (\text{solid})$$
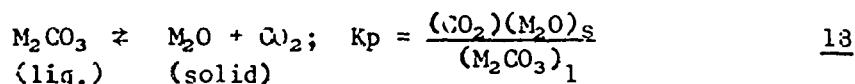
or

$$\frac{\Delta G^0}{RT} = - \ln Kp = pCO_2 \qquad \underline{19}$$

if the chemical potentials of M_2CO_3 and M_2O are each unity. It should be recalled that the (pO^{-2}, pCO_2) scales are functions of the properties of the individual solvent systems (e.g., Table 7a). In Table 8 are summarized the values of pCO_2 at which various oxides will precipitate from the ternary carbonate eutectic at 600°C. Saturation solubility was assumed to be about 10^{-5} molal in each case. From eq. 19, it is seen that the precipitation pCO_2 values may be considered as pK_b or pK_a values since oxides may be basic or acidic.

The reaction of magnesia in molten carbonates, a basic oxide, would be governed by:

$$MgO + CO_2 \rightleftarrows Mg^{+2} + CO_3^{-2}; \quad K_b = \frac{(Mg^{+2})(CO_3^{-3})}{(MgO)(CO_2)} \qquad \underline{20}$$
$$(\text{base}) \quad (\text{acid})$$
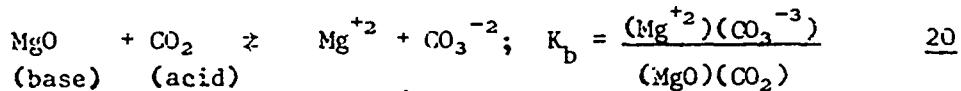
and that of SiO_2, an acidic oxide, by:

$$SiO_2 + Na_2CO_3 \rightleftarrows Na_2SiO_3 + CO_2; \quad K_a = \frac{(SiO_3^{-2})(CO_2)}{(CO_3^{-2})(SiO_2)} \qquad \underline{21}$$
(acid) (base)
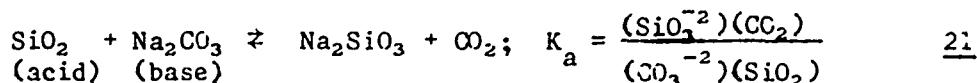
Inspection of the precipitation pCO_2 values (Table 8) shows that for MgO, log K_b = - 2.8, whereas for SiO_2, log K_a = 24.6; the values are in accord with the known excellent properties of high purity MgO as a container material for molten carbonates and the inability of silica glass to withstand attack or corrosion by molten carbonates. High purity alumina has been reported[42] to withstand carbonate attack, especially after pretreatment of the Al_2O_3 with a small

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(42) G. H. J. Broers and G. G. Piepers; Advanced Energy Conversion, 4, 131 (1964).

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quantity of molten carbonate for a few days. It is of interest to note that a value of - 1.37 is predicted for log K_a governing the precipitation-dissolution reaction for this oxide in molten carbonates, i.e., it should have quite superior properties for the containment of molten carbonates.

Water: Consideration of the role of water in contact with molten carbonates is of interest to further the understanding of the hydrolysis reactions and properties of H^+, OH^-, and H_2O in such media. The following salient generalizations summarize some viewpoints advanced by Dubois[32] and Busson, Palous, Millet and Buvet[36] in this area.

The amphoteric properties of water in contact with molten carbonates may be expressed as:

$$2OH^- \rightleftharpoons H_2O + O^{-2}; \quad K_a = \frac{pCO_2(OH^-)^2}{\pi_{H_2O}}$$

$$2OH^- + CO_2 \rightleftharpoons CO_3^{-2} + H_2O; \quad K_b = \frac{\pi_{H_2O}(O^{-2})}{(OH^-)^2} \qquad \underline{22}$$

It was experimentally observed that the ternary carbonate eutectic (600 °C), with OH^- added (as LiOH) did not evolve H_2O when maintained under a dry argon atmosphere, but rapidly evolved H_2O (equivalent to the added OH^-) when the atmosphere was dry CO_2, i.e., OH^- in molten carbonates has weakly basic properties.

If the variation of the composition of the molten carbonate solvent system is monitored by a reversible oxygen electrode, i.e.;

$$O_2 + 2\,CO_2 + 4e^- \rightleftharpoons 2\,CO_3^{-2} \qquad \underline{23}$$
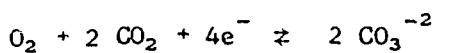
the emf relationship would be:

$$E = E^0 + \frac{2.3RT}{4F} \log \pi_{O_2}\,\pi^2_{CO_2} \qquad \underline{24}$$

It follows from the properties of H_2O (eq. 22) that the emf of an oxygen electrode in a buffered (H_2O/OH^-) carbonate melt would be given by:

$$E = E_0 - \frac{2.3RT}{2F}\,pK_a + \frac{2.3RT}{2F}\log\frac{\pi^2_{H_2O}}{(OH^-)^2} + \frac{2.3RT}{4F}\log\pi_{O_2} \qquad \underline{25}$$

i.e. a linear dependence of E as a function of π_{H_2O} and a theoretical slope of 86 mv. for 1 logarithmic unit of π_{H_2O} are predicted. Further, from the temperature dependence of the emf, the enthalpy change

for the hydrolysis reaction:

$$CO_3^{-2} + H_2O \rightleftarrows CO_2 + 2OH^- \qquad \underline{26}$$
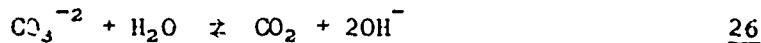
can be established. The investigations of Busson, Palous, Millet and Buvet[36] in the ternary buffered carbonate melt have confirmed the theoretically predicted dependence of E on π_{H_2O}, and in the temperature range, $600° - 750°C$, the value of ΔH^0 for the above ''decomposition'' reaction of the carbonate solvent is found to be 21 ± 2 kcal mol^{-1}. This value is to be compared with the value 78 and 60 kcal mol^{-1} for the process:

$$M_2CO_3 {}_{(liq)} \rightleftarrows M_2O {}_{(liq)} + CO_2 \qquad \underline{27}$$
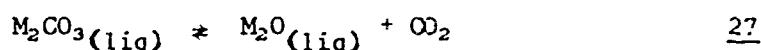
calculated from the CO_2 equilibrium dissociation pressures of the anhydrous carbonates[43], Li_2CO_3, Na_2CO_3, and 27 kcal mol^{-1} from the dissociation pressures of the molten ternary eutectic carbonate mixture[44]. The latter value appears unusually low, and may indicate a promotion of CO_2 evolution by possible traces of water in

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(43) G. J. Janz and M. R. Lorenz; J. Chem. Eng. Data $\underline{9}$, 94 (1964).

(44) P. L. Spedding and R. Mills:, J. Electrochem. Soc., $\underline{112}$, 594 (1965).

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the ''anhydrous'' eutectic mixture; additional studies appear of interest to resolve this point.

If the acidity of the molten carbonates lies in the region where OH^- is the thermodynamically stable form (i.e. $- \log \pi_{CO_2} \gtreqqless 1.5$) and the melt is in contact with hydrogen as well as H_2O, the emf

of the oxygen electrode is given by[36]:

$$E = E^o + \frac{2.3Rf}{F} \log \pi_{CO_2} + \frac{2.3RT}{2F} \log \frac{(OH^-)^2}{\pi_{H_2}} \qquad \underline{28}$$

in accord with the oxidation:

$$H_2 + 2CO_3^{-2} \rightleftarrows 2e^- + 2CO_2 + 2OH^- \qquad \underline{29}$$
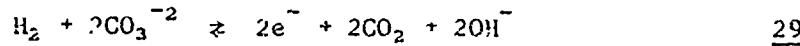
A linear slope of 173 mv (i.e. $\frac{-2.3RT}{F}$) is predicted for the variation of E with $-\log \pi_{CO_2}$ at 600°C; this is twice the value (86 mv) predicted for the preceding region. This inflexion in the slope at a value of $-\log \pi_{CO_2} = 1.5$ has been confirmed experimentally[36].

Corrosion: For aqueous systems, Pourbaix[45] has considered the problems of corrosion and passivity, and has shown that

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(45) M. Pourbaix; Thermodynamics of Dilute Aquious Solutions; Arnold Publishing Co., London (1949).

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the terms of the pH vs. redox potential may be used for diagrammatic representation of the principle features of each system. Littlewood[46] extended these principles to the water analogous acidity functions for molten chlorides, i.e. the pO^{-2} function, where it is assumed that the oxide ion activity may arise from various sources, such as the addition of oxides, or factors such

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(46) R. Littlewood; J. Electrochem. Soc. <u>109</u>, 525 (1962); R. Littlewood and C. Edeleanu; <u>Silicates Industriels</u>, <u>26</u>, 447 (1961).

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as glass container and melt hydrolysis. The criterion of corrosion is that a substance will <u>tend</u> to dissolve or oxidize (i.e. corrode) if the reversible Nernst potential for this substance is more ''active'' than the pO^{-2} redox potential of the molten salt solvent system. When equilibrium is re-established, all the redox systems will have the same potential, i.e. the substance will continue to corrode until the redox potential of the melt and the reversible potential of this substance in the melt have identical values. The principles of this approach to the problems of corrosion in the molten carbonates, as reported by Ingram and Janz elsewhere[33], may be summarized as follows.

The redox potential in the carbonate melt will depend on the pressures of CO_2 and O_2 in the gas phase; thus the oxidation of CO_3^{-2} may be expressed as:

$$CO_3^{-2} - 2e^- \rightarrow CO_2 + \frac{1}{2} O_2 \qquad \underline{30}$$
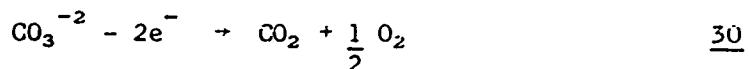
If the CO_3^{-2} ion activity is close to unity, it follows that

$$E_{redox} = E^0 - 2.3 \frac{RT}{2F} pCO_2 + 2.3 \frac{RT}{4F} \log (O_2) \qquad \underline{31}$$

for the anhydrous melt. It has been established that this relation is accurately obeyed; a convenient reference scale of potential is thus established if E is arbitrarily equated to zero[47] for the most ''noble'' mixture of CO_2 and O_2 at 1 atm total pressure (i.e. when

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(47) This convention differs from that of the standard hydrogen electrode, where it is that E^0 is zero at any T. With the assumption above, $E^0 = 0.0413$ mv. rather than zero at 600 °C for $P_{O_2} = \frac{1}{3}$ $P_{CO_2} = \frac{2}{3}$ atm respectively.

$CO_2 : O_2 = 2:1$). Following this convention, the expression for E_{redox}, at 600 °C, is:

$$E_{redox} = 0.0359 - 0.086 \, pCO_2 + 0.0433 \log (O_2) \qquad \underline{32}$$

If the partial pressures of CO_2 and O_2 are known, the properties of the system are uniquely defined. The diagrammatic representation of the thermodynamics of metal-molten carbonate systems, discussed elsewhere in detail[33], is illustrated in Fig. 2 for Ni in contact with the molten carbonate eutectic at 600 °C. Inspection shows that the diagram develops the information as three domains of behavior: immunity (i.e. virgin metal), corrosion (M^{n+}) and one where the corrosion product is the insoluble oxide (and in which there exists the possibility of passivation). A comparison of some predictions and experimental observations for Au, Pt, Ag, stainless steel, and Ni in the ternary carbonate eutectic at 600 °C is shown in Table 9. The results of some potentiostatic studies of the properties of stainless steel in the molten ternary carbonate eutectic at 600 °C are illustrated in Fig. 3; the passivation loop is clearly evident. It is understood that the thermodynamic approach gives no insight into the kinetics of the corrosion processes; the merit of this method lies in the perspective gained relative to the conditions under which the metals can be immune or passive, and the prediction of primary passive potentials[48].

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(48) For additional studies in this area see also: Dubois (ref. 32) and Busson, Palous, Rivet, and Millet (ref. 34), carbonates; Bartlett and Johnson (ref. 35), carbonates, sulfates, nitrates; and A. Conte and S. Cassadeo; La ricerca sci., 36, 433, 488 (1966), nitrates.

Electrolysis of Carbonates: Some general features of the
current-voltage curve for the decomposition electrolysis[39] of the
ternary carbonate eutectic are illustrated in Fig. 4. The line AB
corresponds to the anodic process, e.g., the oxidation of the CO_3^{-2}
ion:

$$CO_3^{-2} - 2e^- \rightarrow CO_2 + \frac{1}{2} O_2 \qquad \underline{33}$$
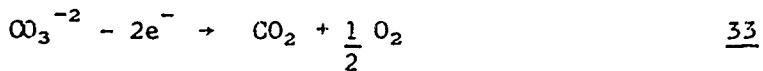
whereas the range BC is the range of electroactivity of the electro-
lyte. The latter is an important property in the consideration of
fused salts as high temperature electrolyte solvents; the span of
electroactivity is governed by the processes leading to melt decom-
position. In the present illustration, the portion CD, commencing
at - 2.5 v is the cathodic breakdown of the electrolyte. In this
electrolysis, substantial deposits of carbon are observed.

The cathodic deposition of carbon from molten electrolytes had
been noted by Haber and Tolloczko[49] as early as 1904 in the elec-
trolysis of mixtures of $BaCO_3$ and $BaCl_2$ at 580 °C. The observation,
that the processes of carbon deposition are markedly enhanced if
Li^+ or Ba^{+2} ions are components of the molten electrolytes was re-
ported more recently (1944) by Andrieux and Weiss[50]; the work
was directed to an electrochemical route for the synthesis of inor-
ganic carbides utilizing mixtures of chlorides and carbonates as

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(49) F. Haber and S. Tolloczko; Z. anorg. Chem. 41, 407 (1904).

(50) J. L. Andrieux and G. Weiss; Compt. rendu (Paris) 219, 551 (1944).

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solvent electrolytes. In the past two decades, the interest of the studies of the electrode processes has centered on the relevance of these to high temperature fuel cells, corrosion, and the electro-chemical recovery of breathing oxygen from carbon dioxide; it is of interest to note that carbon has been frequently reported as the cathodic product in such electrolysis [32, 33, 36, 38 – 40, 51, 52, 53].

(51) J. Dubois and R. Buvet; Bull. Soc. Chem. (France) 2522 (1963).

(52) Yu K. Delimarskii, V. F. Gresclanko, and A. V. Goodynskii, Ukr. Zh. 31, 32 (1965).

(53) G. J. Janz and A. Conte; Electrochemica Acta 9, 1279 (1964).

Some of the possible factors relevant to these observations have been examined from the thermodynamic viewpoint by Ingram, Baron and Janz [39]. Three possible cathodic processes in the molten carbonate electrolysis were considered:

(i) the deposition of the alkali metal:
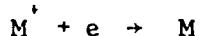
$$M^+ + e \rightarrow M \qquad \underline{34}$$

(ii) the formation of carbon by the electro-reduction of CO_2:

$$3CO_2 + 4e^- - C + 2CO_3^{-2} \qquad \underline{35}$$

(iii) the formation of CO by the electro-reduction of CO_2:

$$2CO_2 + 2e^- \rightarrow CO + CO_3^{-2} \qquad \underline{36}$$

where (ii) and (iii) could equally well have been expressed as $CO_3^{-2} + 2e^- \rightarrow CO + 2O^{-2}$, respectively. The observed cathodic potentials relative to the electrolytic deposition of carbon in

three different molten carbonate media, and the thermodynamically predicted standard electrode potentials for the preceding processes are summarized in Table 10.

The following points may be noted. In the ternary eutectic (600 °C) the cathodic potential at which carbon is observed is - 2.5 v, i.e., about 0.93 v more negative than the predicted E^o for the CO_2/C electrode. Interpreting this ''overpotential'' as due to an increase in oxide ion activity the local acidity of the cathodic environment is predicted to be:

$$\Delta E = - 0.75 \frac{(2.3RT)}{F} \quad pCO_2 \qquad (a)$$

or

$$pCO_2 = 5.5 \qquad (b)$$

Anodic stripping coulometry of the deposited carbon established that the oxide concentration within the above carbon deposit was 1.7×10^{-2} M. This is to be compared with 1.2×10^{-2} M, the value of the oxide ion concentration found by Busson, Palous, Buvet, and Millet (34) for the ternary carbonate eutectic at 600 °C and an acidity of $pCO_2 = 5.5$.

A consideration of the thermodynamic acidity scales of the three electrolytes (Table 7), shows that the change of acidity for Li_2CO_3 and $(Na,K)CO_3$ relative to the ternary eutectic (750 °C) is 2.8 and 2.0 units of pCO_2, respectively (mol fraction scale). The corresponding changes in potentials due to differing acidities, from eq. 37a, are + 0.42 and - 0.3 v. The predicted cathodic potentials for C deposition, relative to the potential observed in the elec-

trolysis of the ternary eutectic are summarized in Table 10 c. The
value predicted for the Li_2CO_3 electrolysis is in good accord with
the observed value (- 1.88 and - 1.97 v respectively); for the
$(Na,K)CO_3$ electrolysis, the predicted value, - 2.65 v, is greater
than the first of the two observed values, - 2.25 and 2.70 v. It
is suggested that at - 2.25 v, liberation of the alkali metal to
an extent sufficient to amalgamate the surface of the Au cathode
occurs and that at - 2.70 v, the appearance of free alkali metal
occurs (c.f. $E^0(Na^+,Na)$ - 2.80 v. 750°C, Table 10 b). The presence
of Na as a cathodic product was chemically confirmed[39]; the exact
correspondence of the anodic stripping potential peak with the cath-
odic deposition peak (Fig. 4 b) are support for the reversibility
of alkali metal deposition in the carbonate electrolyte. The note-
able absence of carbon as a cathodic product is thus understood as
being thermodynamically denied, i.e., the theoretical potential for
C deposition (- 2.65 v) is greater than that for the first appear-
ance of alkali metal (- 2.25 v).

   Similar considerations[39] relative to the formation of carbon
monoxide from the cathodic reduction of the carbonate electrolyte
(eq. 36) show that in a medium of $pCO_2 = 5.5$, the predicted CO_2 CO
equilibrium potential is - 2.55 v. The carbon monoxide electrode
is thus 0.25 v more negative than the corresponding carbon electrode
(ternary eutectic electrolysis, 600°C); carbon deposition with high
current efficiencies, accordingly, would be predicted from this
viewpoint. Under favorable conditions, current efficiencies as

high as 97% were observed[39]. In the presence of a CO_2 atmosphere

the carbon deposition current efficiency decreases (e.g. 60 - 70%);

this suggests the participation of the Boudouard reaction:

$$C + CO_2 \; \rightleftharpoons \; 2CO \qquad\qquad \underline{38}$$

since this favors carbon monoxide formation as the temperatures ap-

proach 700°C. This was confirmed experimentally by withdrawing an

electro-deposit of carbon to a position just above the molten car-

bonate in a CO_2 atmosphere; at 600°C, the carbon disappeared over

a period of hours; at 700°C, the disappearance was complete after

a few minutes.

While the over-all situation is undoubtedly more complex, it

is noteworthy that the principle features of the observed cathodic

phenomena in molten carbonate electrolysis may be rationalized in

terms of the acid-base concepts and the thermodynamic method[33, 39].

The cathodic behaviour is undoubtedly influenced greatly by the dif-

fusion of oxide ions, and by the growth of the carbon deposit; add-

itional discussion[54, 55] is difficult without further experimental

advances in this area of molten carbonate electrochemistry.

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(54) The primary deposition of the alkali metals, with subsequent
chemical reduction of the carbonate ions, viz:

$$M_2CO_3 + 4M \; \rightleftharpoons \; C + 3M_2O$$
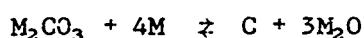
is not ruled out. The free enthalpy change predicted at 1000°K
for the above process and for the free enthalpy of formation
for the oxides are:

M:		Li	Na	K
ΔG^0 (kcal mol^{-1})		-ve	approx zero	+ve
$\Delta G^0_{f_{M_2O}}$ (kcal mol^{-1})		-94	5	47

Thus it is clear that the cathodic carbon deposition can be directly related to the thermodynamic stabilities predicted for the alkali metal oxides (G. H. J. Broers (Amsterdam), private communication to G. J. J., 1956).

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(55) For the application of the thermodynamic method to the problems of the extractive oxygen electrolysis of molten mixtures of halides, hydroxides, and carbonates, see W. E. Arnoldi, ref. 40.

Acknowledgments

Table 1

General Properties of Some Fused Salts, Water and Carbon Tetrachloride

Property \ System	NaF	NaCl	$NaNO_3$	Na_2CO_3	$HgCl_2$	$ZnCl_2$	H_2O	CCl_4
m(°C)	995°	808°	310°	854°	277°	283°	0°	-24°
b(°C)	1704°	1465°	(d)[+]	(d)[++]	304°	732°	100°	77°
density g cm³	1.94	1.55	1.90	1.97	4.36	2.46	1.00	1.59
viscosity (cp)	–	1.38	2.88	3.41	1.74	2900	1.00	0.97
surface tension (dyne cm^{-1})	201	117	116	211	–	–	72.0	28.0
specific conductance ($ohm^{-1} cm^{-1}$)	4.94	3.60	1.01	2.90	3×10^{-5}	4×10^{-2}	4×10^{-8}	4×10^{-18}
ΔS_{fusion} (cal deg^{-1} $mole^{-1}$)	6.25	6.38	6.4[*]	5.9	7.5	10.0	5.25	2.6
ΔS_{vap} (cal deg^{-1}) $mole^{-1}$	29	24	–	–	24	32	26	21

Footnotes: [+]decomposes approx. 380°C; [++]thermal dissociation to M_2O and CO_2

[*]ΔS_f for $NaNO_3$ includes $\Delta S_{e.u.}$ = 0.3 for solid state transition

Table 2

Melting Points and Compositions of Fused Salt Eutectics

Eutectic Mixture A – B – C	Composition (mol%)		Melting Point (°C)
	A	B	
LiCl-KCl	59.5	40.5	352°
NaNO$_3$-KNO$_3$	50	50	220°
Li$_2$CO$_3$-K$_2$CO$_3$	62	38	488°
Li$_2$CO$_3$-K$_2$CO$_3$	43	57	498°
Li$_2$CO$_3$-Na$_2$CO$_3$	53	47	500°
Na$_2$CO$_3$-K$_2$CO$_3$	56	44	710°
Li$_2$CO$_3$-Na$_2$CO$_3$-K$_2$CO$_3$	43.5	31.5	397°
KCl-KF-K$_2$CO$_3$	42.9	34.3	528°
LiF-NaF-KF	46.5	11.5	454°

Table 3

Species and Characteristic Vibrational Frequency

Assignments For Molten $ZnCl_2$ and Molten $HgCl_2$

Species	Frequency (cm^{-1})	Ref.
$(ZnCl_2)n$	75, 226, 250, 360	5
(polymer)	95, 230	4
$(ZnCl_2)_n^{2-n}$ (discrete molecules)	110, 266	4
$HgCl_2$	100, 313, 376	
$HgCl_3^-$ *	210, 282, 287	7
$HgCl_4^{-2}$ *	180, 192, 267, 276	

*These species were not observable in molten
$HgCl_2$ unless Cl^- (as KCl) was added in excess.

Table 4

Values of the Parameters, E_Λ and E_η, for Some Molten Electrolytes

(kcal mole^{-1})	LiF	LiCl	LiBr	LiI	LiNO$_3$	Li$_2$CO$_3$
E_Λ	1.78_4	2.01_5	2.11_7	1.29_5	3.58_5	4.43_8
E_η	-	7.00_7	5.35_5	4.42_3	5.10_3	16.89_3
	NaF	NaCl	NaBr	NaI	NaNO$_3$	Na$_2$CO$_3$
E_Λ	2.96_4	2.99_0	3.22_8	3.22_1	3.21_5	4.19_9
E_η	-	9.30_8	5.13_2	5.67_3	3.88_6	26.26_0
	KF	KCl	KBr	KI	KNO$_3$	K$_2$CO$_3$
E_Λ	2.49_5	3.41_5	3.74_7	3.44_2	3.57_7	4.65_0
E_η	-	6.58_6	5.16_1	5.34_3	4.30_1	29.48_7
	RbF	RbCl	RbBr	RbI	RbNO$_3$	Rb$_2$CO$_3$
E_Λ	-	4.40_1	4.17_1	3.99_9	3.49_6	-
E_η	-	6.09_4	4.86_3	5.16_5	-	-
	CsF	CsCl	CsBr	CsI	CsNO$_3$	Cs$_2$CO$_3$
E_Λ	3.26_2	5.11_6	5.53_3	5.45_0	3.68_8	-
E_η	-	5.68_7	-	5.70_6	-	-

Table 5

Equivalent Conductance For Molten Nitrates, Carbonates,

and Chlorides At Common Reference Temperatures

Cation \ Anion	Cl^-	CO_3^{-2}	NO_3^-
	(Equivalent Conductance $(ohm^{-1}\ cm^2\ equiv.^{-1})$)		
			*
Li^+	180	81	136 (44)
Na^+	152	89	166 (55)
K^+	121	80	139 (45)
Rb^+	100	-	98 (33)
Cs^+	87	-	80 (46)

Footnotes: [+] The reference temperature is taken as 10% above the melting point (°K) of the molten chloride.

* The values in parentheses are the observed conductances for the nitrates at 10% above the melting points (°K) of the respective nitrates.

Table 6

Extractive Electrolyses[(a)]

Electrolyte	T(°C)	Electrode Product
$(Na_2O, 2GeO_2)$, NaF	1000	Ge (99.8%)
GeO_2, $Na_2B_4O_7$	1000	
(NiO, GeO_2), NaF	1000	$(Ni-Ge)_x$
SiO_2, K_2O, GeO_2	1100	Ge (99.99%)
SiO_2, Na_2O, GeO_2	1100	Ge (99.2%)
GeO_2, $(4SiO_2, 3Li_2O)$	1250	$(Ge-Si)_x$
GeO_2, $Na_2B_4O_7$, Na_2AsO_4	800	$(Ge-As)_x$
NiO, B_2O_3, MgO, MgF_2	1200	NiB; Ni_2B
KF, KBF_4, CoO	900	CoB, Co_2B, Co
KF, VCl_3	800	V (99.5%)
KF, KBF_4, MoO_3	950	B, Mo_2B_5, MoB
KF, KBF_4, WO_3	950	B, W_2B_5, WB
KF, K_2SiF_6, KBF_4	950	SiB_3

[(a)] From references (i - vii)

(i) J.L. Andrieux and M.J. Barbier-Andrieux, Compt. Rend., 240, 2104 (1935).

(ii) M.J. Barbier-Andrieux, Compt. Rend., 242, 2352 (1956).

(iii) M.J. Barbier-Andrieux, Bull. Soc. Chim. France, 241, 309 (1955).

(iv) S. Aleonard, Bull. Soc. Chim. France, 827 (1958).

(v) S. Aleonard, Bull. Soc. Chim. France, 653 (1960).

(vi) S. Aleonard, Bull. Soc. Chim. France, 34, (1961).

(vii) A. Ruis, F. Colom, and A. Artacho; Electrochimica Acta, 11, 1497 (1966).

Table 7

Domains of Acidity In Molten Carbonates[32,33,34,39]

(a) <u>Basic limit;</u> $(0^{-2}) = 1.0$ (referred to the pure molten oxide as the reference state).

	Ternary Eutectic	$(Na,K)CO_3(50:50)$	Li_2CO_3
600°C	11.0	-	-
750°C	8.5	10.5	5.7

(b) Basic limit;

$(0^{-2}) = 1.0$, referred to molten carbonate with $(0^{-2}) = 1$ mol 1^{-1}

Acid limit;

$(CO^{-2}) = 1.0$, referred to molten carbonate with $(CO_2) = 1$ mol 1^{-1}

t(°C)	500°C	600°C	700°C
Ternary Eutectic	8.9	7.5	6.7

Table 8

" Precipitation" pCO_2 Values for Various

Oxides in the Molten Ternary Carbonate Eutectic at 600°C[34]

Oxide	pCO_2	Oxide	pCO_2	Oxide	pCO_2
BaO	5.50	Li_2O	6.09	Au_2O_3	(4.50)*
CaO	2.27	Na_2O	10.9	Mn_2O_3	-2.18
Al_2O_3	1.37	K_2O	15.0	ZnO	-4.79
MgO	-2.18	PtO	(-5.24)*	FeO	-4.34
SiO_2	-24.6	Ag_2O	-4.50	CoO	-5.52

(*)
  Values in parenthesis indicate approximations.

Table 9

Corrosion Behaviour of Selected Metals in the Ternary

Eutectic at 600°C[a]

Metal	Theoretical 'domain'	Experimental[b]
Au	immune	no corrosion, no oxide
Pt	immune or oxide-cover	passive
Ag	corrosion	corrodes to Ag+
Fe (stainless steel)	oxide-cover	passive
Ni	oxide-cover	corrodes to NiO

(a) From M. D. Ingram and G. J. Janz, see refer. 33.

(b) Refer: G. J. Janz, A. Conte and E. Neuenschwander,
Corrosion 19, 292t (1963); G. J. Janz and A. Conte,
Corrosion 20, 238t (1964), Electrochim. Acta, 9, 1269
(1964), ibid, 9, 1279 (1964).

Table 10

Electrolytic Deposition of Carbon From Fused Carbonates[39]

(a) Observed Cathodic Potentials (volts)

Electrolyte:	ternary eutectic	$(Na,K)CO_3$	Li_2CO_3
600°C	-2.5		
750°C	-2.3	-2.25; -2.7	-1.97
Comment	carbon deposit	no carbon deposit	carbon deposit

(b) Standard Electrode Potentials[*] (volts)

E°	Li^+/Li	Na^+/Na	K^+/K	CO_2/C	CO_2/CO
600°C	-3.44	-3.00	-3.02	-1.56	-1.61
750°C	-3.23	-2.80	-2.82	-1.55	-1.53

(c) Predicted Cathodic Potentials (volts) for C Deposition

Electrolyte:	ternary eutectic	$(Na,K)CO_3$	Li_2CO_3
750°C	-2.3 (obsv.)	-2.65	-1.88

(*)
Relative to the Danner-Ray Reference Electrode: $[Ag/Ag^+(Li,K) SO_4/porcelain/CO_3^{-2}]$

Figure 1: Temperature-Composition Diagrams for Liquid-Solid
           Equilibria in Carbonate Systems.

           A - C: Binary Systems (see ref. 1 - 4); D: Ternary

System; Eutectic, m. 397°C; mol %: Li_2CO_3, 43.5; Na_2CO_3, 31.5;

K_2CO_3, 25.0 (see ref. 1, 4).

References:

1. G. J. Janz and M. R. Lorenz; J. Chem. Eng. Data; 6, 321 (1961)
   for Fig. A, B, and D. (ternary eutectic, m.pt. 397°C; composition
   (mol %): Li_2CO_3: Na_2CO_3: K_2CO_3 is 43.5 : 31.5 : 25.0).

2. E. J. Cairns and D. I. MacDonald; Nature, 194, 441 (1962)
   for insert in B.

3. A. Riesman; J. Amer. Chem. Soc. 81, 807 (1959) for C.

4. M. Rolin and J. M. Recapet; Bull. Soc. Chim. France; 2104
   (1964) for somewhat different results for C; also for D (ternary
   eutectic, m.pt. 392°C; comp. (mol %): Li_2CO_3: Na_2CO_3: K_2CO_3 is
   42.5 : 30.6 : 26.9).

Figure A: Phase diagram, $T, °C$ vs Mole % Li_2CO_3, between K_2CO_3 and Li_2CO_3.

Figure B: Phase diagram, $T, °C$ vs Mole % Li_2CO_3, between Na_2CO_3 and Li_2CO_3, with inset showing detail between 50 and 54 near 505.

Figure C: Phase diagram, $T, °C$ vs Mole % Na_2CO_3, between K_2CO_3 and Na_2CO_3, showing regions α, $\alpha + \gamma$, γ.

Figure D: Ternary phase diagram Na_2CO_3 – Li_2CO_3 – K_2CO_3 with isotherms at 800°, 700°, 600°, 500°, 400°.
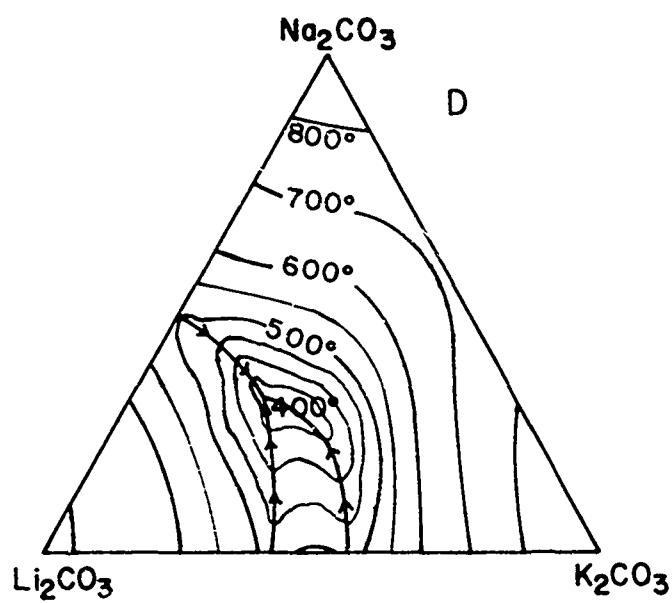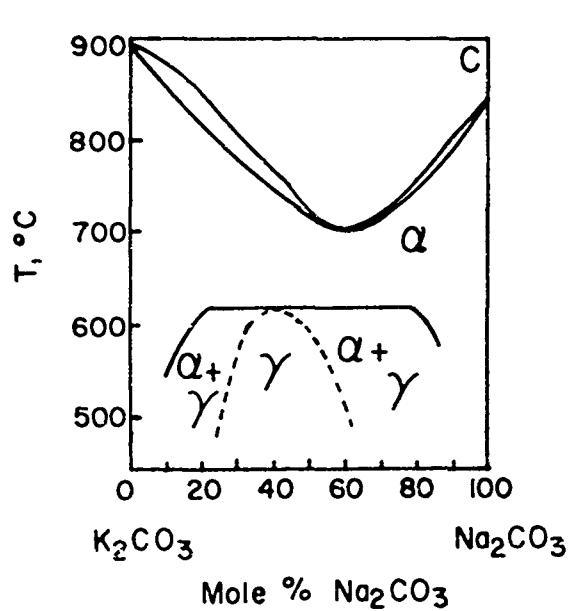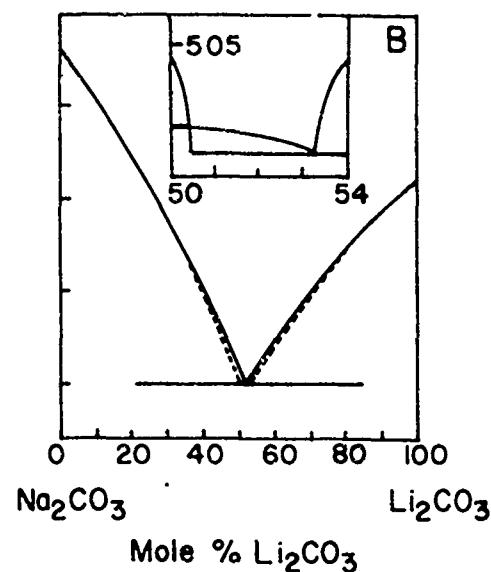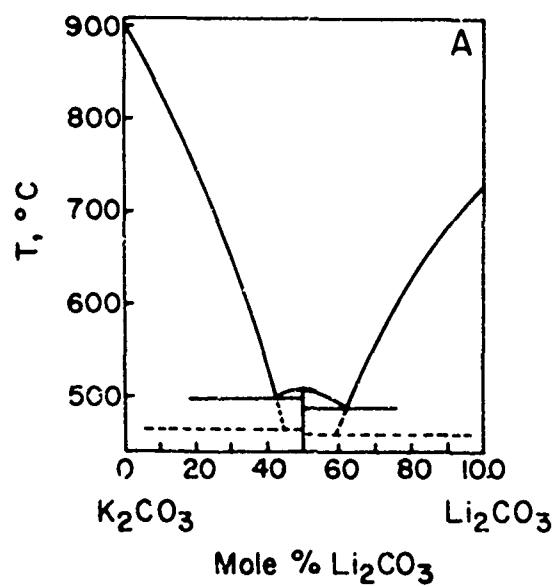
FIGURE 2

E|pCO$_2$ Diagram For The System Nickel-Ternary Eutectic at 600 °C
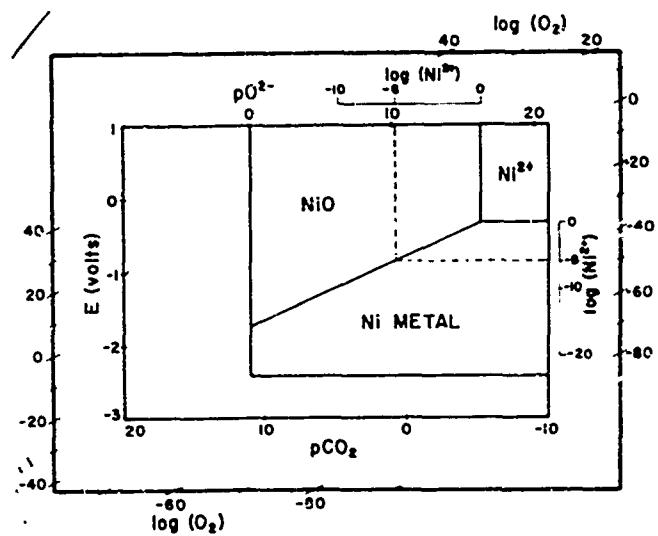
If nickel metal were immersed in the carbonate melt under an atmosphere of carbon dioxide (e.g. ''normal operating conditions,'' 0.9 atm CO$_2$ and 0.1 atm O$_2$) i.e., (pCO$_2$, 0; E, 0, O$_2$; i.e. pCO$_2$, 0; E, 0) . This would approximate a the point on the diagram in the region of oxide-cover. Since the concentration of Ni^{2+} ions in the melt at this point is as low as 10^{-5}M, two possibilities exist: either the metal will corrode completely to oxide; or the NiO will form a coherent film on the metal surface and lead to passivation. The thermodynamic treatment cannot distinguish these two possibilities. Inspection of this diagram also shows that at a CO$_2$ pressure of 10^5 atm (i.e. O$_2$ pressure, 10^{-19} atm) oxide formation becomes thermodynamically unfeasible. It is also seen that if the reduction of the potential of Ni is reduced to -0.8 V under normal conditions, the metal should be rendered immune.

Figure 3: Anodic Potentiostatic Polarization Curves For Type 347 Stainless Steel In The Ternary Carbonate Eutectic [a]

The curves a and b are, respectively, for tube and rod shaped specimens; temperature 600 °C; CO_2, 1 atm press.

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a. See ref. 52.

_____
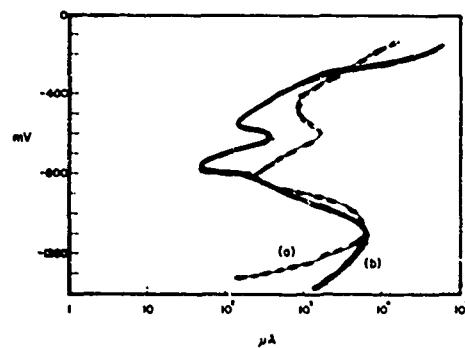
Figure 4:   Current-Voltage Curve in The Ternary Carbonate Eutectic

At 600 °C [a]

Curves I and II are for the electrolyses under CO_2 and Argon atmospheres, respectively.   The solid line is the cathodic sweep; the dashed line, the anodic sweep.

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a. See ref. 39.

Potential, V
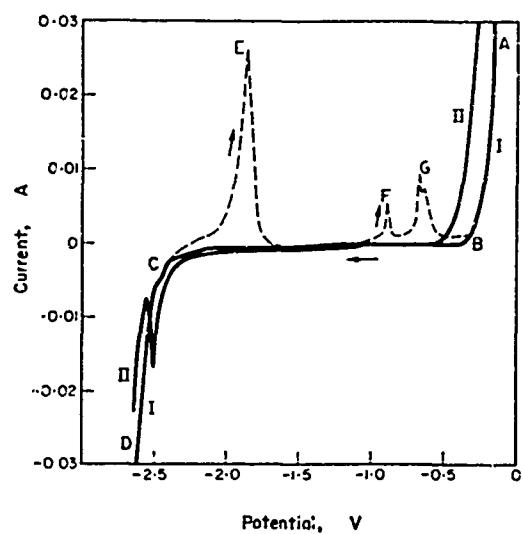
Appendix

Molten Carbonate Electrolytes As Solvent System

Physico-Chemical and Electrochemical Data

A 1. Melting Points, Boiling Points
A 2. Binary Eutectic Mixtures
A 3. Ternary Eutectic Mixtures
A 4. Cryoscopic Constants and Results
A 5. Cryoscopic Constants of Eutectic Mixtures
A 6. Equilibrium CO_2 Dissociation Pressures
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A 8. Heat Capacities
A 9. Heats and Entropies of Fusion
A10. Densities
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A14. Electrical Conductance
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A17. Diffusion of Various Ionic Species As Solutes
A18. Thermodynamic Emf Series and CO_2-oxide Precipitation Values
A19. Polarographic Data
A20. Electrolytic Carbide Formation
A21. Reference Electrodes
A22. Emf series: Danner-Rey Reference Electrode Scale
A23. Corrosion Processes
A24. Diagrammatic Representation of Corrosion Principles
A25. Static Corrosion Studies
A26. Silver Solubility in Molten Carbonates
A27. Stainless Steel Passivation
A28. Corrosion Potentials for Various Metals
A29. Electrolytic Dissolution of Au, Pt, Au-Pd in Molten Carbonates
A30. Corrosion Behaviour: Comparison of Theoretical Prediction With Experiment
A31. Containment of Carbonates
A32. Fuel Cells and Related Studies
A33. Miscellaneous Data

Table A1: Melting Points and Boiling Points of Some Carbonates[a]

Carbonate	mp(°C)	bp(°C)
Li_2CO_3	735	d590
Na_2CO_3	854	d600
K_2CO_3	896	d670
Rb_2CO_3		d700
Cs_2CO_3		d775
Ag_2CO_3		
$BeCO_3$		d (1 atm 25°)
[1]$MgCO_3$		
[2]$CaCO_3$	1340	
[3]$SrCO_3$	1497	
[4]$BaCO_3$		
$ZnCO_3$		d150 (1 atm 350)
$CdCO_3$		d327 (1 atm 350)
$HgCO_3$		
Tl_2CO_3	273	d230
$PbCO_3$		d315, or (1 atm 300)
$MnCO_3$		d < 100?
[5]$FeCO_3$		
$CoCO_3$		d ≫ 140

Stability: [1]0.1 mm 400, 1 atm 540. [2]0.1 mm 500,
1 atm 900. [3]1 atm 1289. [4]0.2 mm 900,
1 atm 1360. [5]1 atm 282.

(a) in part from: Molten Salt Handbook, G.J.Janz; Academic Press Inc. N.Y. (1967)

Table A2: Binary Eutectic Mixtures[a]

m.pt. (°C)	System A	System B	Composition A (mol %)	m.pt. (°C)	System A	System B	Composition A (mol %)
250°	$LiNO_3$	Li_2CO_3	98.1	672°	K_2SO_4	Na_2CO_3	34
283°	Na_2CO_3	NaOH	7.2	678°	KF	K_2CO_3	60
292°	Cs_2CO_3	CsOH	10.3	686°	$BaCO_3$	Na_2CO_3	37
304°	$NaNO_3$	Na_2CO_3	97.6	686°	KF	K_2CO_3	48
326°	KNO_3	K_2CO_3	96	690°	NaF	Na_2CO_3	38.7–40
442°	Li_2CO_3	LiOH	10.2	710°	K_2CO_3	Na_2CO_3	44
488°	K_2CO_3	Li_2CO_3	38	734°	NaCl	$BaCO_3$	53
498°	K_2CO_3	Li_2CO_3	57.3	785°	$CaCO_3$	Na_2CO_3	40
50?°	LiCl	Li_2CO_3	61	~790°	$CaCO_3$	K_2CO_3	~60
500°	Li_2CO_3	Na_2CO_3	53	794°	Nb_2O_5	K_2CO_3	11
530°	CsF	Cs_2CO_3	57	814°	NaCl	$BaCO_3$	76
568°	NaF	K_2CO_3	51	820°m	Na_2SO_4	Na_2CO_3	~/.°
588°	KCl	Na_2CO_3	55.6	826°	Na_2CO_3	$BaTiO_3$	98.6
608°	LiF	Li_2CO_3	49	845°	Nb_2O_5	K_2CO_2	33.5
616°	RbF	Rb_2CO_3	66	860°	$BaCl_2$	$BaCO_3$	82.5
622°	$CaCl_2$	$CaCO_3$	70	1090°	Ta_2O_5	K_2CO_3	32.3
627°	RbF	Rb_2CO_3	49	1150°	Nb_2O_5	K_2CO_3	65
634°	NaCl	Na_2CO_3	76.9				
636°	KCl	K_2CO_3	65				
653°	$CaCO_3$	$Ca(OH)_2$	35.8				
655°	Na_2CrO_4	Na_2CO_3	52.2				
662°	$CaCO_3$	Li_2CO_3	32.8				

(a), in part, from: Physical Properties of Fused Salt Mixtures,P.V. Clark; AEC Report SC-R-65-93? V.1 (Sandia,1965); Clearinghouse for Federal Scientific and Technical Information, U. S.Dept.Commerce, Springfield,Va., and from ''Molten Salt Handbook, G.J.Janz; Academic Press, Inc. N.Y. (1967).

Table A3: Ternary Eutectic Mixtures[a]

m.pt. (°C)	System			Composition (mol%)		
	A	B	C	A	B	C
282°	NaCl	Na_2CO_3	NaOH	7.8	6.4	85.8
397°	K_2CO_3	Li_2CO_3	Na_2CO_3	25.0	43.5	31.5
455°	LiCl	Li_2SO_4	Li_2CO_3	52.9	27.2	19.8
528°	KCl	KF	K_2CO_3	42.9	34.3	22.7
546°	KCl	K_2SO_4	Na_2CO_3	47.3	34.0	18.7
558°	KCl	K_2CO_3	Na_2CO_3	42.5	43.3	18.1
558°	KF	NaF	K_2CO_3	8	30	62
560°	KCl	NaCl	Na_2CO_3	36.8	36.2	27.0
562°	NaF	K_2CO_3	Na_2CO_3	32	42	26
575°	KBr	NaBr	Na_2CO_3	38.1	42.9	19
575°	NaCl	NaF	Na_2CO_3	42.5	20.5	37
612°m	NaCl	Na_2SO_4	Na_2CO_3	51.8	24.1	24.1
658°	NaF	Na_2CO_3	Na_2SO_4	37.4	37.4	25.2
805°m	$CaCO_3$	K_2CO_2	Na_2CO_3	50	37	13
811°	$BaCl_2$	$BaCO_3$	$BaTiO_3$	79.5	11.3	9.2

Table A4: Cryoscopic Studies[a]

Solvent	Cryoscopic[a] Constant	Solutes	Freezing Point Depression Factor	Ref.
Na_2CO_3	39.9	(a) $NaCl$;$NaOH$;Na_2O; (b) Li_2CO_3; K_2CO_3 (c) KCl,$LiCl$; KOH; (d) $BaCl_2$	(a) $n = 1$ (b) $n = 2$ (c) $n = 3$ (d) $n = 4$	1
Li_2CO_3	13.60	Na_2CO_3		7
$SrCO_3$		SrO	-	8
$CaCO_3$		$Ca(OH)_2$	-	3,4
$NaCl$	20.40	Na_2CO_3; $SrCO_3$	$n = 1$; $n = 2$ (ideal)	9
KCl	25.40	K_2CO_3	$n = 1$ (ideal)	10
$BaCl_2$	161.2	$BaCO_3$	ideal	2
KF	21.86	K_2CO_3	ideal	5
NaF	16.69	Na_2CO_3	ideal	
KBr	39.29	K_2CO_3		6
$NaNO_3$	16.13	Na_2CO_3	$n = 1$ (ideal)	11
$Ca(OH)_2$	-	$CaCO_3$		3,4

(a) in part from: Molten Salt Handbook, G. J. Janz; Academic Press,Inc. N. Y. (1967).

1. M.Rolin and J.M.Recapat; Bull.Soc.Chim.,France, 2511 (1964)
2. O. Sackur; Z.phys. Chem., 78, 550 (1912)
3. R.S.Bradley, Am. J. Sci., 260, 374 (1962)
4. J.Lumsden; Thermodynamics of Molten Salt Mixtures; Academic Press, N.Y. (1966)
5. M.Amadori; Atti. Accad. naz. Lincei Rc., 22II, 366 (1913)
6. R.Cohen- Adad, M.Michaud, J. Saïd, and A.P. Rollet; Bull. Soc. Chim. France 356 (1961)
7. C.Sinistri and P.Franzosini; Ricerca Scient.(ii) A3,449 (1963)
8. E.H. Baker; J. Chem. Soc. 339 (1963)
9. P.H.J. Hoenen; Z. physik. Chem., 83, 513 (1913)
10. G.Petit and C. Bourlange; Compt. rendu., 237, 457 (1953)
11. E.P. Van Artsdalen; J. Phys. Chem, 60, 172 (1956)

Table A5

Cryoscopic Constants of Mixtures

	K_f[a]	Ref.
Li_2CO_3, K_2CO_3(eutectic)	14.6_6	1
Na_2CO_3, K_2CO_3(min.melting sol'n)	49.0_8	1
Li_2CO_3, Na_2CO_3, K_2CO_3(eutectic)	13.5_2	2

(a) units: deg. $mole^{-1}$ kg^{-1}

1. G.J.Janz and J.L. Perano; Trans. Faraday Soc., 60, 1742 (1960).

2. G.J.Janz, E. Neuenschwander, and F.J. Kelly; Trans. Faraday Soc., 59, 841 (1963).

Table A6: Equilibrium CO_2 Dissociation Pressures of Molten Carbonates[a]

Li_2CO_3

$t(°C)$	735	776	797	82i	843
pCO_2 (mm Hg[1])	11.6	53.2	111	247	501

Na_2CO_3

$t(°C)$	840	855	885	950[2]
pCO_2 (mm Hg[1])	0	8	15	9

$(Li,Na,K)CO_3$ eutectic

$t(°C)$	750	800	850	900	950
pCO_2 (mm Hg[3])	10.5	24	46	72	108

ΔH (kcal mole^{-1})[b] Li_2CO_3: 7δ; Na_2CO_3: 60; tern. eutectic, 27.

(a) in part from: Molten Salt Handbook, G. J. Janz; Academic Press, Inc., N. Y.(1967); (b) calc'd from vapor pressure data in this table for $M_2CO_3 \rightleftharpoons M_2O + CO_2$.

[1]G.J. Janz and M.R. Lorenz, J. Chem. Eng. Data 9, 94 (1964). See also, J.T. Howarth and W.E. S. Turner, J. Soc. Glass Technol. 14, 394 (1930); ibid, 15, 360 (1931); J. Johnston, Z. Physik. Chem. 62, 330 (1908); P. Lebeau, Ann. Chim. Phys. 6, 422 (1905).

[2]Value at 950°C from P.L. Spedding and R. Mils, J. Electrochem. Sec. 112, 594 (1965).

[3]P.L. Spedding and R. Mils, J. Electrochem. Soc. 112, 594 (1965).

TABLE A7. Oxygen and Carbon Dioxide Solubilities in Molten Carbonates

a. Oxygen

Molten carbonate (eutectic)	Henry's Law Constant, K (moles O_2 / cm^3atm)	ΔH (kcal / mole)
$(Li,K,Na)CO_3$[‡,a]	log K= -2.47 - 3860 / T(°K)	17.7
$(Li,Na)CO_3$[a]	log K= -3.20 - 3260 / T	14.9

b. Carbon Dioxide in the Ternary Eutectic

t(°C)	Solubility $S(10^3)$ (moles CO_2 / cm^3)	Henry's law constant, K (mole / cm^3atm)
560[b]	0.1	0.9(± 0.1) x 10^{-1}
500[a]	too low for	-
600[a]	detection by thermo-balance owing to	-
700[a]	interfering dissociation	-
800[a]		-

[a] M. Schenke, G. H. J. Broers, and J. A. A. Ketelaar, J. Electrochem. Soc. 113, 404 (1966); Also private communication, G. H. J. Broers to G. J. Janz (1966).

[b] J. Dubois, Ph.D. Thesis, Fac. Science, Univ. Paris (1964).

‡ Saturating pressure, 1 atm (CO_2; O_2); partial pressures, O_2, 0.1-0.9 atm.

Table A8: Coefficients of Molar Enthalpy and Heat Capacity Functions[a]

$$\Delta H = aT + bT^2 - c \; ; \; Cp = a + bT$$

System	Phase	Range (°K)	a	$b \times 10^3$	$c \times 10^{-3}$
Li_2CO_3	S	560–996	3.82	21.37	1.28
	L	996–1150	30.85	6.77	3.04
Na_2CO_3	S	707–1127	8.14	17.65	0.04
	L	1127–1210	33.99	5.35	7.28
K_2CO_3	S	630–1169	19.19	13.03	6.38
	L	1169–1250	36–95	5.32	10.05

Mixtures

Composition

Li_2CO_3–K_2CO_3	S	457–778	33.82	–	–11.24
(50–50 mole %)	L	778–1200	44.65	–	–10.96
(m.505°C)					
Na_2CO_3–K_2CO_3	S	440–628	34.24	–	–10.98
(56–44 mole %)	S	628–695	43.50	–	–16.71
(m.710°C)	S	695–758	65.05	–	–31.64
	S	758–983	47.63	–	–17.82
	L	983–1197	44.26	–	– 9.84
Li_2CO_3–Na_2CO_3–K_2CO_3	S	540–670	6.95	24.68	3.95
(43.5–31.5–25.0	L	670–1100	28.41	8.28	4.32
mol %)(m.397°C)					

(a) G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc., 59, 841 (1963). G. J. Janz and J. L. Perano, ibid., 60, 1742 (1960).

See also: M. Rolin and J. M. Recapet, Bull. Soc. Chim. France, 2504 (1964).

Table A9: Heats and Entropies of Fusion[a]

Single - Salts

Salt	m.p.,°C	ΔH_f kcal mole^{-1}	ΔS_f cal deg.$^{-1}$ mole^{-1}
Li_2CO_3	726	10.7 ± 0.1	10.7 ± 0.1
Na_2CO_3	858	6.7 ± 0.2	5.9 ± 0.2
K_2CO_3	898	6.6 ± 0.1	5.6 ± 0.1

Mixtures

Composition (mol %)	m.p.,°C	ΔH_{tr} (cal mole^{-1})	ΔH_f (kcal mole^{-1})	ΔS_f (cal mole^{-1} deg.$^{-1}$)
Li_2CO_3 – K_2CO_3 50 50	505	–	8.7 ± 0.1	11.2 ± 0.1
Na_2CO_3 – K_2CO_3 56 44	355	*(88)		
	422	*(55)		
	485	606		
	710	–	4.7 ± 0.1	4.7 ± 0.1
Li_2CO_3 – Na_2CO_3 – K_2CO_3 43.5 31.5 25.0	397	–	6.6 ± 0.1	9.9 ± 0.1

* The brackets indicate that these values were not gained directly from the graphs but were calculated from the enthalpy data.

(a) G. J. Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc., 59, 841 (1963); G. J. Janz and J. L. Perano, ibid., 60, 1742 (1960).

See also: M. Rolin and J. M. Recapet, Bull Soc. Chim. France, 2504 (1964); for additional recent results: e.g., $\Delta H_{fus.}$: Li_2CO_3, about 9 kcal mole^{-1}; ternary eutectic, about 6.5 kcal mole^{-1}.

TABLE A10: Densities of Molten Carbonates

$$\rho = a-bT \ (g \ cm^{-3})$$

Salt	mp($^\circ$K)	a	b $\times$ 10^3	Range ($^\circ$K)	Ref.
Li_2CO_3	891	2.2026	0.3729	1010-1120	
Na_2CO_3	1131	2.4797	0.4487	1140-1280	1
K_2CO_3	1172	2.4141	0.4421	1180-1280	

Melt Densities (Mixtures)

$$\rho = a-bT \ (g \ cm^{-3})$$

	a	b $\times$ 10^3	σ^*	Ref
$Li_2CO_3-Na_2CO_3$	2.4560	0.5188	0.0021	
$Li_2CO_3-K_2CO_3$	2.5108	0.5992	0.0086	2
$Na_2CO_3-K_2CO_3$	2.4734	0.4828	0.0031	
$Li_2CO_3-Na_2CO_3-K_2CO_3$	2.3644	0.5441	0.0151	

$*$ σ is the standard deviation.

Additional Studies

	Ref.
$NaOH-NaCl-Na_2CO_3$	3

References

1. G. J. Janz and M.R. Lorenz, J. Electrochem. Soc. 108, 1052 (1961).

2. A. T. Ward and G. J. Janz, Electrochimica Acta, 10, 849 (1965).

3. J. Lasek, Collection Czech. Chem. Commun., 29, 1958 (1964).

Table A11: Surface Tensions of Molten Carbonates

$$\gamma = a - bT \text{ (dynes/cm)}$$

Salt	mp(°K)	a	b	Standard deviation(±)	Range(°K)	Ref.
Li_2CO_3	891	284.7	0.0407	1.3	1030-1140	
Na_2CO_3	1131	269.8	0.0514	0.7	1150-1300	1
K_2CO_3	1172	244.4	0.0042	0.5	1180-1300	

System	Comp. (mol %)					
$Li_2CO_3-Na_2CO_3$	43.3: 46.7	313.5	0.0766	1.1	890-1050	
$Li_2CO_3-K_2CO_3$	42.7: 47.3	325.0	0.1257	1.7	867-1110	
$Na_2CO_3-K_2CO_3$	58.0: 42.0	289.4	0.0773	0.4	1040-1180	2
$Li_2CO_3-Na_2CO_3-K_2CO_3$	43.5: 31.5: 25.0	268.1	0.0694	1.0	697-1090	

1. G.J.Janz, E. Neuenschwander and F. J. Kelly, Trans. Faraday Soc., 59, 841 (1963).

2. G.J.Janz and J. L. Perano, ibid., 60, 1742 (1960).

See also: G.K. Moisiev and G.K. Stepanov: Reports (Trudy) Inst. Electrochem., Ural'sk Akad. Nauk. SSR. No.5 (1964) and No.6 (1964) for surface tensions of molten carbonates, including Ca_2CO_3.

Table A12: Heats of Mixing for Binary Mixtures of Fused Salts

System	$4 \Delta H_{mi: 0.5}$	Ref.
$Na_2(CO_3-SO_4)$	0	1
$Na_2(CO_3-S)$	+3750	2
$(Na_2-Ca)CO_3$	-2370	
$(K_2-Ca)CO_3$	-5700	3
$(Na,K-Ca)CO_3$	-4190	

1. H. Flood, T. Forland, and K. Motzfeldt; Acta Chem.Scand. 6, 257 (1952).

2. E. Rosen and L.G. Sillen; ibid; 14, 692 (1960).

3. T. Forland; Norg. Tek, Vitenskapsakad., Series 2,No.4 (1957).

Table A13: Excess Partial Free Energies of Mixing[a]

System	Excess Partial Free Energy $RT\ln \gamma = kN^2_X n+$
$Li(CO_3)_{0.5}$ $[\underline{Na}(CO_3)_{0.5}:1]$	$-1200\ N^2_{Na}+$
$Li(CO_3)_{0.5}$ $[\underline{K}(CO_3)_{0.5}:1]$	$-3700\ N^2_K+$
$NaF(Na_2CO_3:1)$	$-400\ (1-N_F-)^2/(2-N_F-)^2$
$NaCl(Na_2CO_3:1)$	$-400\ (1-N_{Cl}-)^2/(2-N_{Cl}-)^2$
$KF(K_2CO_3:1)$	$-1600\ (1-N_F-)^2/(2-N_F-)^2$
$KCl(K_2CO_3:1)$	$-400\ (1-N_{Cl}-)^2/(2-N_{Cl}-)^2$
$KBr(K_2CO_3:1)$	$-400\ (1-N_{Br}-)^2/(2-N_{Br}-)^2$
$Li_2CO_3(LiOH:1)$	$-1600\ N^2_{OH}-/(2-N_{OH}-)^2$
$Na_2CO_3(NaOH:1)$	$-1800\ N^2_{OH}-/(2-N_{OH}-)^2$
$SrCO_3(SrO:1)$	$-4300\ N^2_O-2$
$CaCO_3(Na(CO_3)_{0.5}:1)$	$-2500\ N^2_{Na}+/(1+N_{Ca}+2)^2$
$CaCO_3(K(CO_3)_{0.5}:1)$	$-5500\ N^2_K+/(1+N_{Ca}+)^2$
$Na(CO_3)_{0.5}$ $[K(CO_3)_{0.5}:1]$	0.00
$CaCO_3(CaO:1)$	$-2800\ N^2_O-2$
$CaCO_3(Li(CO_3)_{0.5}:1)$	$-600\ N^2_{Li}+2/(2-N_{Li}+2)^2$
$CaCO_3(Ca_{0.5}OH:1)$	$200\ N^2_{OH}-/(2-N_{OH}-)^2$

(a) In part from, Thermodynamics of Molten Salt Mixtures; J. Lumsden,
Academic Press, London and New York (1966).

Table A14 : Electrical Conductance of Molten Carbonates[a][1,2]

Specific Conductance, $\varkappa = A_{\varkappa} e^{-E_{\varkappa}/RT}$ (ohms^{-1} cm^{-1})

	$A_{\varkappa}$	$E_{\varkappa}^{\dagger}$	s	Range (°K)
Li_2CO_3	29.34	3.954	0.00198	1018–1118
Na_2CO_3	13.758	3.527	0.0042	1138–1240
K_2CO_3	11.027	3.941	':0.0017	1184–1279
Li_2CO_3-Na_2CO_3	44.43	4.45	0.0052	840–960
	25.70	4.01	0.0019	1050–1160
Li_2CO_3-K_2CO_3	44.60	6.88	0.0051	850–990
	19.69	5.27	0.0022	990–1150
Na_2CO_3-K_2CO_3	15.84	4.52	0.0015	1040–1160
	420.3	9.66	0.0301	670–740
Li_2CO_3-Na_2CO_3-K_2CO_3	38.86	6.00	0.0063	840–1020

Equivalent Conductance. $\Lambda = A_{\Lambda} e^{-E_{\Lambda}/RT}$ (ohms^{-1} cm^2 equiv.$^{-1}$)

	A_{Λ}	$E_{\Lambda}^{\dagger}$	s	Range (°K)
Li_2CO_3	754.5	4.438	–	1018–1,
Na_2CO_3	550.2	4.199	0.035	1138–1240
K_2CO_3	544.6	4.650	0.0175	1184–1279
Li_2CO_3-Na_2CO_3	655.7	4.69	0.0019	1050–1160
Li_2CO_3-K_2CO_3	821.1	6.00	0.0030	990–1150
Na_2CO_3-K_2CO_3	642.5	5.13	0.0017	1040–1160
Li_2CO_3-Na_2CO_3-K_2CO_3	1244.5	6.46	0.0069	840–1020

$\dagger$units: kcal mole^{-1}; s, stand ' deviation.

(a) In part from: Molten Salt   ook, G. J. Janz; Academic Press, N. Y. (1967).

1. G. J. Janz and M. R. Lorenz, J. Electrochem. Soc. 108, 1052 (1961).

2. A. T. Ward and G. J. Jarz, Electrochimica Acta 10, 849 (1965).

Table A15: Viscosities of Molten Carbonates[1][‡]

$$\tau_1 = Ae^{E/RT} \quad (cp.)$$

	A(10^3)	E	$s^{\#}$	Range ($^\circ$K)
Li_2CO_3	1.406	16,893	0.1057	1050-1120
Na_2CO_3	0.0383	26,260	0.0112	1160-1240
K_2CO_3	0.0116	29,487	0.0207	1190-1250

$$\eta = a + bT + cT^2 + dT^3 \quad (cp.)$$

	a	b(10^2)	c(10^4)	d(10^8)	$s^{\#}$	Range ($^\circ$K)
Li_2CO_3	-4259.12	1480.91	-138.58	431.294	0.0792	1050-1120
Na_2CO_3	1464.54	-344.322	27.0982	-71.3260	0.00804	1160-1240
K_2CO_3	2117.23	-496.107	38.8776	-101.829	0.0157	1190-1250

$s^{\#}$ = Standard deviation

$Li_2CO_3-Na_2CO_3-K_2CO_3$ $\tau_1 = 4.65 \times 10^{-3} \, e^{(11,000/RT)}$ cp.   700°-900°K
(mol %: 43.5: 31.5: 25.0)

Additional Studies	Ref.
B_2O_3 with carbonates of (Li,Na,K,Rb,Cs)	2
NaOH-NaCl-Na_2CO_3	3

Ref. 1. G. J. Janz and F. Saegusa; J. Electrochem. Soc. 110, 452 (1963).

2. R. Kruh and K. Stern; J. Amer. Chem. Soc. 78, 278 (1956).

3. J. Lasek; Collection Czech. Chem. Commun. 29, 1858 (1964).

[‡] For somewhat different results see the data reported by G. V. Voroliev, S. F. Pal'guev, and S. V. Karpachev; Trudy No. 6 (1965) Inst. Electrochem. Urals. Acad. Sci., English Transl. Electrochem.Solid and Liq. Electrolytes, Vol. 3, p. 33 (1966) Consultants Bureau, New York.

Table A16: Tracer Diffusion in Molten Carbonates[1]

(a) Tracer Diffusion Coefficient, $D = A e^{-E/RT}$ $(cm^2 sec^{-1})$

System	Diffusing Species	$A(10^3)$	E(kcal mol^{-1})	Range (°C)
Na_2CO_3	$*Na^+$	10.0	12.17	900° – 1062°
	$*CO_3^{-2}$	2.86	10.62	
Li_2CO_3	$*Na^+$	1.32	9.63	810° – 990°
	$*CO_3^{-2}$	1.35	9.74	
$(Li,Na)CO_3$	$*Na^+$	4.42	10.06	757° – 938°
(75:25)	$*CO_3^{-2}$	3.57	10.92	
eutectic	$*Na^+$	9.81	10.99	570° – 853°
	$*CO_3^{-2}$	7.36	11.56	
(25:75)	$*Na^+$	9.40	11.91	778° – 932°
	$*CO_3^{-2}$	4.26	11.13	
$(Li,K)CO_3$	$*K^+$	7.26	11.49	575° – 860°
(eutectic)	$*CO_3^{-2}$	7.94	11.86	
$(Na,K)CO_3$	$*Na^+$	8.18	11.82	756° – 965°
(eutectic)	$*K^+$	7.61	11.84	
	$*CO_3^{-2}$	2.71	11.03	
$(Li,Na,K)CO_3$	$*Na^+$	8.06	11.035	420° – 860°
(eutectic)	$*CO_3^{-2}$	1.58	10.070	
	$*K^+$	9.73	11.880	

(1) P. L. Spedding and R. Mills; J. Electrochem. Soc., 112, 594 (1965); 113, 599 (1966); J. Phys. Chem. 70, 4077 (1966).

Table A17: Diffusion of Various Ions in Molten Carbonates[a,b]

(a) K_2CO_3 - Li_2CO_3 eutectic; (640°C)

Species	Conc.(10^3) (g.eg.cm^{-3})	D(10^5) (cm²sec^{-1})	Species	Conc.(10^3) (g.eg.cm^{-3})	D(10^5) (cm²sec^{-1})
Pb^{+2}	0.021	2.74	Cr^{+6}	0.045	4.12
Ni^{+2}	0.010	4.89	Cl^-	1.3	0.089_1
Cu^{+2}	0.023	3.78	Br^-	1.2	0.081_2
Cd^{+2}	0.028	2.71	I^-	1.8	0.071_5

(b) K_2CO_3 - Na_2CO_3 eutectic; (710°C)

Species	Conc.(10^3) (g.eg.cm^{-3})	D(10^5) (cm²sec^{-1})	Species	Conc.(10^3) (g.eg.cm^{-3})	D(10^5) (cm²sec^{-1})
Cd^{+2}	-	2.7	Br^-	-	0.081
Cl^-	-	0.089	I^-	-	0.071

(a) N. K. Tumanova; Ukr. Khim. Zhur; 30, 648 (1964);

(b) Y. K. Delimarskii; Euchem. Conf. Molten Salts, Ulvik, Norway (1966).

Table A18: Thermodynamic Emf Series and CO_2-Oxide Precipitation Values

Metal	Electrode $E°,V$ [2]	Oxide pressure $\log(O_2)$ [3]	Oxide precipitation pCO_2 [4]
Ba(II)	-2.90	-56.86	+5.50
Li	-2.87	-54.90	+6.09
Ca	-2.59	-65.20	-2.27
K	-2.45	-27.34	+15.0
Na	-2.43	-35.1	+10.9
Mg	-2.41	-60.80	-2.18
Mn	-1.38	-38.42	-2.88
Zn	-0.89	-31.02	-4.79
Fe(II)	-0.66	-24.70	-4.34
Co	-0.39	-20.88	-5.52
Ni	-0.34	-19.16	-5.24
Pt	(+0.52	+0.28	(-5.24)
Ag	+0.55	+2.48	-4.50
Au	(+0.84)	+9.4	(-4.50)

1. M.D. Ingram and G.J.Janz; Electrochimica Acta; <u>10</u>, 783
    (1965); see also: H.Flood, T.Forland, and K. Motzfeldt;
    Acta Chim. Scand., <u>6</u>, 257 (1952).

2. Emf series relative to E arbitrary zero for the CO_2/O_2
    electrode with $CO_2:O_2 = 2:1$ at a total pressure of 1 atm.
    for: $CO_3^{-2} - 2e^- = CO_2 + K_2O$.

3. Equilibrium partial pressures for oxide dissociation.

4. The values for pCO_2 (= $-\log CO_2$) at which the oxide will
    precipitate from the molten carbonate.

Table A19: Polarographic Data In Molten Carbonates [1-3]

K_2CO_3, Li_2CO_3 solvent (640°C)

Solute	Concentration (moles liter^{-1} x 10^3)	$E_{\frac{1}{2}}$ (volts)	$-\Delta E \Big/ \Delta \log(\frac{i_e-i}{i})$	$\frac{2.3RT}{nF}$
ZnO	0.107-0.3520	0.99-0.945	0.103-0.085	0.0905
CuO	0.1381-0.4620	0.71-0.73	0.180-0.20	0.1810
CdO	0.1069-0.4553	0.95-0.925	0.104-0.11	0.0905
PbO	0.1709-0.5847	0.715-0.76	0.090-0.12	0.0905
KNO_2	38.08-74.18	0.65-0.63	0.107-0.11	0.0905
K_2SO_3	34.15-48.71	0.165-0.170	0.10-0.11	0.0905
Tl_2O_3	0.1799	0.775	0.10	0.0905
(2 waves)		1.15	0.18	0.1810
$K_2Cr_2O_7$	0.2504-0.6658	1.01-1.05	0.20-0.25	0.1810

K_2CO_3, Li_2CO_3 solvent (800°C)

Solute	Concentration (moles liter^{-1} x 10^3)	$E_{\frac{1}{2}}$ (volts)	$-\Delta E \Big/ \Delta \log(\frac{i_e-i}{i})$	$\frac{2.3RT}{nF}$
KCl	93.46-18.84	0.060-0.61	0.21-0.23	0.2268
KBr	76.56-118.8	0.595-0.59	0.21-0.23	0.2268
KI	87.28-127.6	0.515-0.495	0.23-0.22	0.2268

K_2CO_3, Li_2CO_3 solvent (900°C)

Solute	Concentration (moles liter^{-1} x 10^3)	$E_{\frac{1}{2}}$ (volts)	$-\Delta E \Big/ \Delta \log(\frac{i_e-i}{i})$	$\frac{2.3RT}{nF}$
Tl_2O_3	0.1104-0.1673	1.15	0.25	0.2567

1. Yu. K. Delimarskii and N. K. Tumanova; Ukr. Khim. Zhur., 30, 52 (1964).

2. N. K. Tumanova and Yu. K. Delimarskii; Ukr. Khim. Zhur., 30, 796 (1964).

3. N. K. Tumanova and Yu. K. Delimarskii; Ukr. Khim. Zhur., 30, 682 (1964).

Table A20: Electrolytic Carbide Formation

Compound Formed	Electrolyte	Ref.
BaC_2	$BaCO_3 - BaCl_2 - LiCl$	1
	$BaCO_3 - BaCL_2 - NaCl$	1
$CaSi_2$	$CaCO_3 - CaCl_2 - CaF_2 - SiO_2$	2
NiC_2	$Li_2CO_3 - K_2CO_3 - Na_2CO_3$	3

1. J. L. Andrieux, and G. Weiss, Compt. rend., 219, 440 (1944).

2. M. Dodero, Compt. rend., 198, 1593 (1934).

3. M. V. Smirnov, L. A. Tsiovkina, and V. A. Oleeinikova; Trans. (Trudy) No. 6 Inst. Electrochem. (1965), Urals. Acad. Sci., Engl. Transl. p. 61 (1966), Consultants Bur. (1366).

Table A21: Reference Electrodes

Electrode	Junction	Solvent (compn.mole%)		Temp. (°C)	Ref.
Pt, O_2 (5.98%) + CO_2 (36-95%)	Na_2CO_3 (0.5-10%)	Porous MgO	Same as electrode soln.	850-1050°	1
Pt or Au (CO_2,O_2)	(Li,Na,K) CO_3 eutectic	Direct contact of solvent	Same as electrode soln.	600-800°	2,6
Ag	$(Li,K)SO_4$; Ag^+(0.1m)	Pythagoras Porcelain	Molten carbonates	500-1000°	3
C (CO_2,Ar)	$Li(Cl,OH,CO_3)$	Direct contact	Same as electrode soln.	500-800°	4
Au(CO,CO_2)	molten carbonates	Direct contact	Same as electrode soln.	800°	5

References:

1. H. Flood, T. Forland, and K. Motzfeldt, Acta. Chem. Scan 6, 257 (1952).

2. G. J. Janz and F. Saegusa, Electrochimica Acta., 7, 339 (1962).

3. G. Danner and M. Rey, Electrochimica Acta., 4, 274 (1961).

4. W. E. Arnoldi; Chapt. 4 in Atmosphere in Space Cabins and Closed Environments, (K. Kammermeyer, ed.) Appleton-Century-Crofts, Publ. N. Y. (1966).

5. A. Borucka; Abstract 2.23 CITCE 16th Meeting; Budapest, Sept. (1965).

6. G. H. J. Broers, M. Schenke and G. G. Prepers; Adv. Energy Conversion 4, 131 (1964).

Table A22: Emf Series: Danner-Rey Reference Electrode Scale[1]

| Electrode | $E°, V$ | | | |
| | 600°C | | 750°C | |
	Standard Oxygen	Danner-Rey	Standard Oxygen	Danner-Rey
Li+/Li	−2·87	−3·44	−2·66	−3·23
Na+/Na	−2·43	−3·00	−2·23	−2·80
K+/K	−2·45	−3·02	−2·25	−2·82
CO_2/C	−0·99	−1·56	−0·98	−1·55
CO_2/CO	−1·04	−1·61	−0·96	−1·53

(1) G. J. Janz, M. D. Ingram, and B. Baron; Electrochimica Acta, 11, 1629 (1966).

Table A23: Corrosion Processes In Molten Carbonates

Element	Melt	Ref.
Cu,Ni,Fe,Ti,Al	LiOH, NaOH, KOH	1
	Caustic alkali	2
Fe and Alloys (Cr,Ti,Al)	Carbonates	3,4,5
	Chlorides and carbonates of alkali and alkaline earths	6,7
	Na_2CO_3	8,9,10
Pt,Au,Au-Pd	Li_2CO_3, Na_2CO_3, K_2CO_3	10,11,12
Ag	Li_2CO_3, Na_2CO_3, K_2CO_3	9,10,11,13
Ni	Li_2CO_3, Na_2CO_3	9,10,12
Co,Ni, Fe	Molten carbonates	14

1. E.I. Gurovich, Zhur. Priklad.Khim. 32,E-253 (1960).

2. P.L. Kiriliov, F.A., Kozlov,V.I. Subbotin, and N.M.Turchin, Atommaya energiya 8, 30 (1960).

3. V.P. Kochergin and E.G. Kokourova, ZhNKh, 7, 2563 (1962).

4. J. Dubois and R. Buvet, Bull.Soc.Chim. France, 2522 (1963).

5. V.N. Strekalovski, G.V. Burov, and I.N. Ozeryanaya; Trans. (Trudy) Ins . Electrochem. No.6 (1965) Urals Acad. Sciences; Engl. Transl. (1966) Consultants Bureau, N.Y.

6. V.P. Kochergin, L.V. Bormotova, N.M. Pryakhina, and A.P. Asanova, ZhPKh, XXXIV, 1258 (1961).

7. V. Kochergin and G. Stolyarov; Zhur. Priklad. Khim., 29, 730 (1958).

8. M.M. Dodero and M.C. Deports, J. Four electrique et des industri. Electroch. 5, 221 (1959).

9. G.J. Janz and A. Conte; Electrochimica Acta, 9,1269,1279 (1964).

10. G.J. Janz and M.D. Ingram; Electrochimica Acta, 10, 783 (1965)

11. G.J. Janz, A.Conte, and E. Neuenschwander; Corrosion, 19, 292t (1963).

12. G.J.Janz and A. Conte; Corrosion, 20, 273t (1964).

13. G.J. Janz and E. Neuenschwander; Corrosion Science, 3, 177 (1963).

14. H.E. Bartlett and K.E.Johnson,Can.J.Chem., 44, 2199 (1966).

Table A24: Diagrammatic Representation of the Thermodynamic Principles Controlling Corrosion Processes for Various Metals in Contact with the Ternary Molten Carbonate Eutectic (600°C).
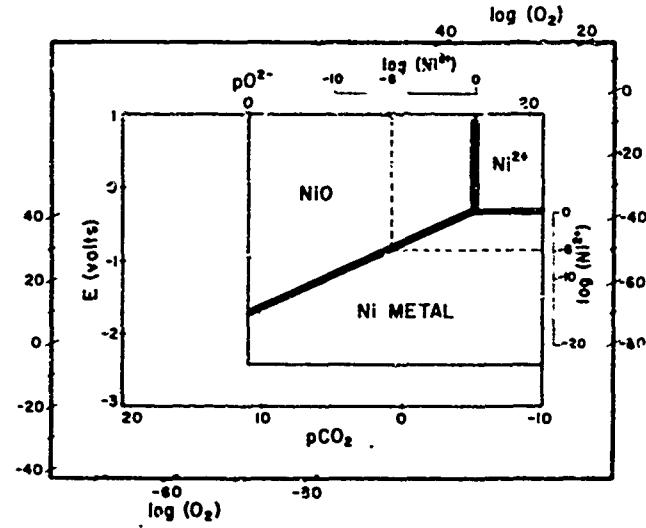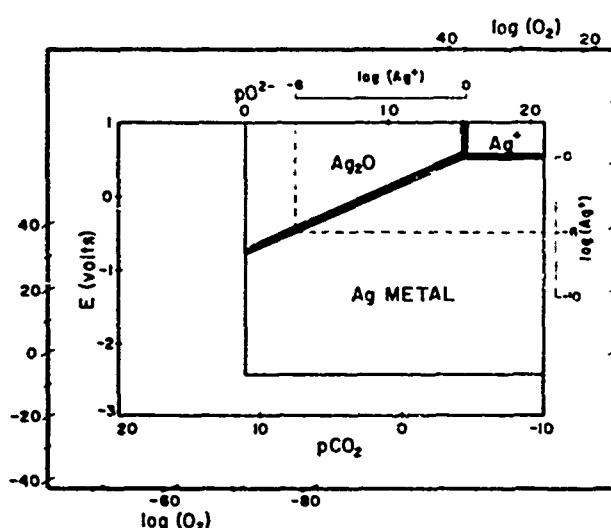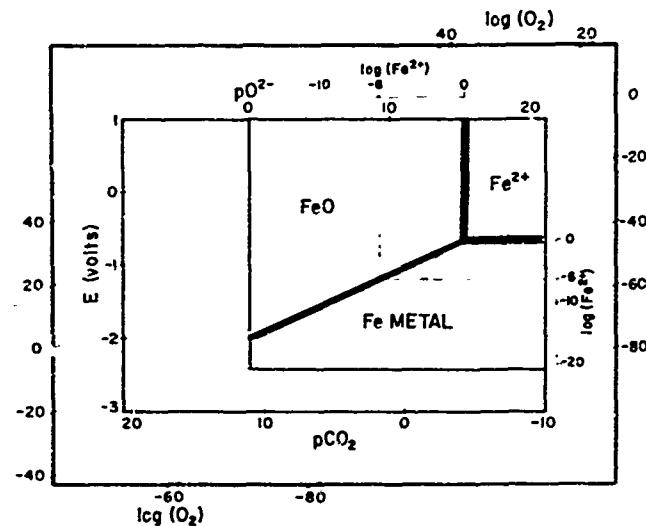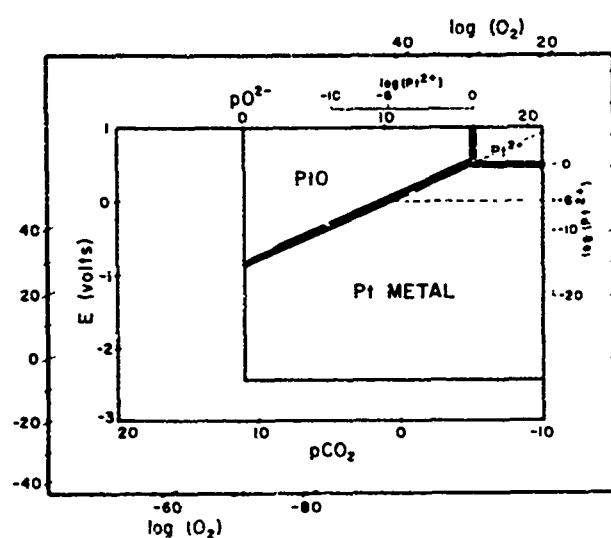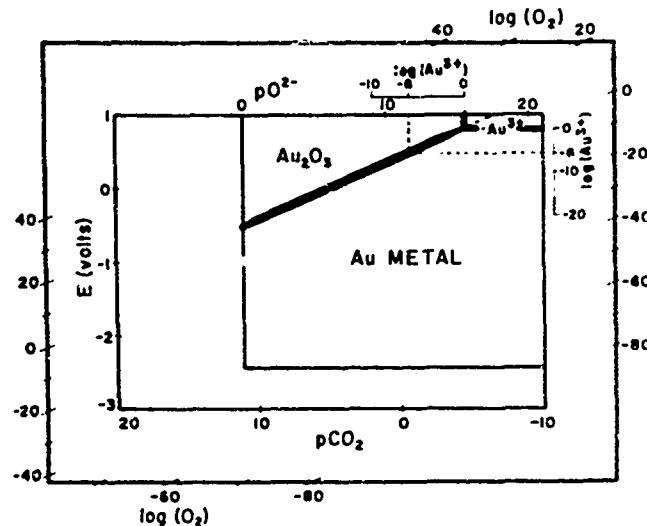
Table A25: Static Corrosion Studies: Pt, Au, Ag, Au-Pd, Ni, Stainless Steel

(a) Static Corrosion Experiments: Pt, Au and Ag in Molten Eutectic Mixture of Li, Na and K Carbonates Under CO_2 Atmosphere[1]

Temp. (°C)	Crucible	Time (hrs)	Foil Surface sq cm.	Sample Change mg/hr/sq cm	mpy
			Platinum		
800°	Au-20% Pd	18	0.9	+0.08	12
820°	Au-20% Pd	6	2.5	<0.03	5
820°*	Au-20% Pd	6	1.2	0.30	48
900°	Au-20% Pd	22	2.0	0.04	6
900°	Au-20% Pd	23	2.0	0.10	16
			Gold		
740°	Sintered Al_2O_3	16	1.36	-0.033	6
840°	Pure Au	16	1.54	-0.045	8
890°	Pure Au	72	1.90	+0.022	4
890°	Sintered Al_2O_3	26	1.80	+0.002	0.4
900°	Pure Au	40	1.85	+0.016	3
910°	Pure Au	3.5	2.10	0.000	0.0
910°	Pure Au	29	2.05	0.017	3
920°	Sintered Al_2O_3	19	2.10	0.015	3
			Silver		
623°	Sintered Al_2O_3	20	1.85	-0.19	62
670°	Au-20% Pd	18	1.00	-1.10	330
720°	Sintered Al_2O_3	23	2.00	-0.09	29
720°	Au-20% Pd	24	0.93	-1.36	450
720°	Pure Au	24	2.35	-1.26	410
720°	Sintered Al_2O_2	17	1.48	-0.23	74
735°*	Au-20% Pd	16	2.18	-0.38	125
740°*	Au-20% Pd	16	1.56	-0.46	150
740°	Sintered Al_2O_3	24	1.93	-0.10	32
790°	Au-20% Pd	18	1.66	-1.83	600
820°	Pure Au	24	2.39	-1.81	590

* Wet CO_2 gas stream; all others, dry CO_2.

(1). G. J. Janz, A. Conte, and E. Neuenschwander; Corrosion, 19, 292t (1963).

Table A25: Static Corrosion Studies: Pt, Au, Ag, Au-Pd, Ni, Stainless Steel

(b) Static Corrosion Experiments: Au-20 Percent Pd Alloy, Nickel and Type
347 Stainless Steel in Molten Li, Na and K Carbonate Eutectic Mixtures
Under CO_2 Atmospheres[2].

Metal	Temperature		Crucible Type	Time (hrs)	Sample Area sq cm	Change mg/hr/sq cm
	°C	°F				
Au-20% Pd	740°	1364°	Sintered Al_2O_3	96	1.90	+0.001
Alloy	740°	1364°	Au-20% Pd	96	2.63	+0.010
Nickel	670°	1238°	Sintered Al_2O_3	63	2.16	-0.010
	670°	1238°	Au	63	2.60	-0.017
Type 347 Stainless Steel	730°	1346°	Sintered Al_2O_3	94	5.0	-0.003
	730°	1346°	Au-20% Pd	95	5.5	+0.023
	730°	1346°	Au-20% Pd	93	8.2*	+0.016

*
The stainless steel sample was galvanically coupled with platinum, both
totally immersed in the melt.

(2). G. J. Janz and A. Conte; Corrosion, 20, 273t (1964).

Table A26: Solubility of Silver in Molten Carbonates[a]

Solvent　　　　　Solubility, X_0 (Ag^+) ($\times 10^4$) [b]

| Solvent	500°C	600°	700°	750°	800°	850°	900°	950°
Li_2CO_3				2.0	2.2	2.4		
$(Li,Na)CO_3$		4.7	5.7	4.9	4.1	3.6	3.3	
$(Li,K)CO_3$		9.9	7.5	6.6	6.2			
$(Na,K)CO_3$					7.3	7.0	6.3	5.5
ternary eutec.	18.7	9.3	7.7	7.0				
Theoretical Prediction (c)	29.0	17.2	11.0	9.1	7.9	6.8	6.0	5.3

(a)　G. H. J. Broers (Amsterdam) private communication to G. J. J. (1967).

(b)　$X_0(Ag^+) = \dfrac{n(Ag^+)}{n(Ag^+)+n(M^+)} = \dfrac{moles(Ag_2CO_3)}{moles(CO_3^{-2})}$; i.e. X_0 is the

Temkin mole fraction at $P_{O_2} + P_{CO_2} = 1$ atm .

(c)　from $\Delta G = 17,500(\pm 2000) - 21.0T + 8.84 \times 10^{-3}T^2 + 0.77 \times 10^5 T^{-1} - 4.76 T \ln T$
(refer: G. J. Janz, E. Neuenschwander and A. Conte; Corrosion Science 3, 177 (1963).

Table A27: Anodic Polarization of Stainless Steel
In Molten Carbonates.[(1)]
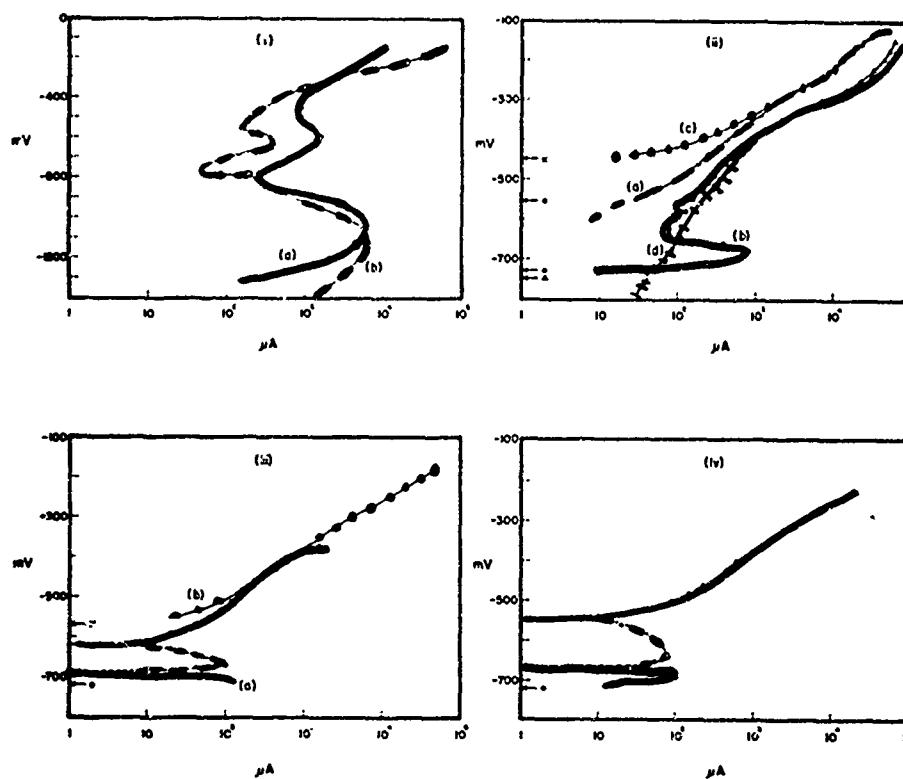
Anodic potentiostatic polarization curves for type 347 stainless steel in fused
carbonates.
(i) specimen as (a) tube and (b) rod, both not equilibrated to corrosion potential (600°C,
CO_2 atm).
(ii) specimen as tube equilibrated to corrosion potential; experiments in the following
order with conditions as specified: (a) 600°C, CO_2; (b) 700°C, CO-; (c) 600°C, CO_2 +
O_2; (d) 600°C, CO; (corrosion potentials marked on left-hand ordinate axis)
(iii) specimen as tube, equilibrated at corrosion potential; (a) a corrosion potential of
−720 mV was initially established (700°C, CO_2), (b) experiment repeated (700°C, CO_2)
with same specimen immediately after the preceding was completed.
(iv) The specimen (tube) was cathodized (8 min, 8 mA) prior to this anodic polarization
curve (700°C, CO_2)

PRIMARY PASSIVE POTENTIALS FOR TYPE 347 STAINLESS STEEL
IN MOLTEN ALKALI CARBONATES

Temperature °C	Potential mV	Remarks
600	-1100, -610	two passive potential were observed for the same anodization [Fig. 2(i)]
600	−610	after cathodic polarization
700	−680	no cathodic loop observed [Fig. 2(ii)]
700	−710	cathodic loop observed [Fig. 2(iii)]
700	690	after cathodic polarization, cathodic loop observed [Fig. 2(iv)]

(1) G. J. Janz and A. Conte; Electrochimica Acta, 9, 1269, 1279 (1964).

Table A28: Corrosion Potentials In Molten Alkali Carbonates at 600°C[1]

Electrode	Potential[‡] (mV)
Au-Pd	-430
Au	-470
Pt	-475
347ss, 304ss	-525 ± (30mV)[‡]
Ag	-680
Ni	-1166

+ Average for all experiments.

‡ Gas bubbling through the melt; dry CO_2; all potentials relative to the Ag/Ag+ reference electrode.

(1) G. J. Janz and A. Conte; Electrochimica Acta 9, 1269, 1279 (1964).

Table A29: Constant Potential Electrolysis In The Li_2CO_2-Na_2CO_3-K_2CO_3 Eutectic[1]

Anode	Temp °C	Time h	Potential (mV)	c.d. mA/cm²	Process considered	Current Efficiency (metal dissolution) %
Au	600	3	-50	83	Au^+	0·02
					Au^{3+}	0·06
Au	700	3	-200	80	Au^+	0·03
					Au^{3+}	0·10
Pt	600	3	-100	40	-	-
Pt	700	3	-100	44	Pt^{2+}	0·02
					Pt^{1+}	0·04
Au-Pd (20%)	600	3	-100	70	Pd^{2+}	0·01
					Pd^{4+}	0·02
Au-Pd (20%)	700	3	-100	86	Pd^{2+}	0·006
					Pd^{4+}	0·01

(1) G. J. Janz and A. Conte; Electrochimica Acta 9, 1269, 1279 (1964).

Appendix

Table A30: Corrosion Behaviour of Selected Metals In The Ternary Eutectic (600°C)

Metal	Theoretical 'domain'[1]	Experimental[2]
Au	immune	no corrosion, no oxide
Pt	immune or oxide-cover	passive
Ag	corrosion	corrodes to Ag^+
(stainless steel)	oxide-cover	passive
Ni	oxide-cover	corrodes to NiO

‡ See Table A24

(1) G. J. Janz and A. Conte; Electrochimica Acta, 9, 1269, 1279 (1964).

(2) G. J. Janz and M. D. Ingram; Electrochimica Acta, 10, 783 (1965).

Table A31: Containment of Molten Carbonates [‡]

Liquid	Temp. °C	Duration	Atmosphere	Material	Remarks
Na_2CO_3	950°	50	CO_2	MgO	6×10^{-3} mg hr^{-1} cm^{-2}
Na_2CO_3	1097°	$\frac{1}{2}$ hr.	CO_2	Pt	
Na_2CO_3-					
K_2CO_3-					
$LiCO_3$	900°	23	CO_2	Pt	10×10^{-2} mg hr^{-1} cm^{-2}
	920°	29	CO_2	Au	1.7×10^{-3} mg hr^{-1} cm^{-2}
	920°	29	CO_2	Au-Pd	as resistant as pure Au
	820°	24	CO_2	Ag	1.8 mg hr^{-1} cm^{-2}
	730°	93	CO_2	Stainless Steel	1.6 mg hr^{-1} cm^{-2}
	670°	63	CO_2	Ni	1.7 mg hr^{-1} cm^{-2}
K_2CO_3	950°	60	CO_2	MgO	8×10^{-3} mg hr^{-1} cm^{-2}
K_2CO_3	1097°	$\frac{1}{2}$ hr.	CO_2	Pt	
Li_2CO_3	780°	60	CO_2	MgO	2×10^{-3} mg hr^{-1} cm^{-2}
Li_2CO_3	1034°	$\frac{1}{2}$ hr.	CO_2	Pt	
Molten Carbonates	700°	extended periods	CO_2, O_2	Al_2O_3 (high purity)	no significant attack, especially after pre-treatment of Al_2O_3 with carbonate melt for a few days (**)

[‡] In part from Molten Salt Handbook (G. J. Janz); Academic Press Inc., Publ. N. Y. (1967).

** See G. H. J. Broers, M. Schenke, and G. G. Prepers; Adv. Energy Conversion 4, 131 (1964).

Table A32: Selected Fuel Cell and Related Studies

Electrodes	Electrolytes	Ref.
Ag, Ni	MgO (70-50 wt.%)- Li,Na.K/CO_3 (30-50 wt.%)	1
Ag,Ni	Molten carbonates (H_2 as fuel)	2
Pt, Au, Ag cathodes	Molten carbonates	3,4,5
C,(Ag,Pt)O_2	Molten carbonates	6
C,(Fe_3O_4)O_2	Molten carbonates	7
Gas Diffusion Electrodes	Molten carbonates	8
H_2-CO(C),(C)O_2	Na,Ba carbonates + halides	9
P(H_2)Ni(CO_2,O_2)	(Li.Na.K)CO_3	10
Miscellaneous		11-25,31
Electrolysis of Molten Carbonates		27,28,29,30

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Table A33: Miscellaneous Studies

(a) Expansivities of Molten Carbonates

	$\alpha \times 10^4$
Li_2CO_3	2.20
Na_2CO_3	2.33
K_2CO_3	2.39

(b) X-Ray and Neutron Diffraction of Molten Carbonates

System	Investigation	Ref.
Li_2CO_3	X-ray (750°-1100°C); liquid state structure and ionic interactions	1
Na_2CO_3		
K_2CO_3		

(c) Volumes of Anions

Anion	Rigid Unit Vol.	Free Rotation Sphere	Ref.
CO_3^{-2}	31.9 $\mathring{A}^3$	76.2 $\mathring{A}^3$	1
SO_4^{-2}	44.5	102.5	1
NO_3^{-}	24.8	51.6	2

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13. ABSTRACT

Because of their applications in fuel cell electrochemistry and in problems such as the electrochemical recovery of breathing oxygen from carbon dioxide, the chemistry and electrochemistry of carbonates in the molten state have been the subject of considerable attention in the period of the past two decades. The concern of the present communication is a survey of the recent contributions in this area, particularly relative to the classification of molten carbonates as solvent systems and as electrolytes. Thermodynamic and transport properties are first considered; a development of the acid-base concept relative to molten carbonates is next examined, and its application to corrosion chemistry and the solubility of oxides in molten carbonates is illustrated. The electrolysis of molten carbonates (cathodic phenomena) is discussed to illustrate the thermodynamic method in this area. A compilation of salient results in the area of molten carbonates is reported as an Appendix of this communication.